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CHARACTERIZATION OF GASOLINES,

DIESEL FUELS

&

THEIR WATER SOLUBLE FRACTIONS

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INTRODUCTION

Characterization of six gasolines and two diesel fuels and their water-soluble fractions (WSF's) by gas chromatography was undertaken to ascertain the types of compounds which may appear in ground water as a result of gasoline contamination. In addition, the diffusion constants for gasoline components into water were estimated thus enabling prediction of the kinetics of dissolution. A bibliography of the open literature on gasoline characterization and toxicity has been included.

MATERIALS AND METHODS

Samples of six gasolines (two regular, two unleaded, and two premium gasolines) and two diesel fuels were purchased at retail outlets [Chevron (Brand A) and Shell (Brand B)] in Oakland, CA, April 7, 1983 and placed in chloroform-rinsed metal solvent cans.

Preparation of water-soluble fractions, WSF's. Tap water, 1890 mL, was placed in a 2 L drain flask and allowed to cool to room temperature, 18°C. Gasoline, 210 mL, was added carefully on top of the water avoiding droplet formation. The mixture was stirred slowly so that the miniscus remained intact. Samples were removed from the drain at the bottom of the flask for ultraviolet spectroscopy, pentane extraction, or headspace analysis. UV spectra were recorded from 350-240 nm. In a preliminary experiment the time dependence to the UV spectra was studied. A plot of the absorbance at 270 nm of Shell regular as a function of time indicated the dissolution was 95% complete in 17.5 hr. Mixtures were stirred for 48 hr to ensure that equilibrium had been reached.

Determination of Dispersion constants. Mixtures of gasolines or diesel fuels with tap water were prepared as above except that the mixtures were not stirred. Formation of the water soluble fraction was followed by UV spectroscopy. Dispersion constants were calculated from the slope of the regression of $Ln[(A_e-A)/A_e]$ on time, where A_e is the extrapolated equilibrium absorbance and A is the absorbance at time, t.

Pentane extraction of WSF's. The aqueous WSF solution, 800 mL, was extracted with 10.0 mL pentane, Burdick & Jackson glass distilled, after the addition of 10 uL dodecane standard and 20 g NaCl. The pentane solution was analyzed by gas chromatography. Each solution was analyzed also without addition of the dodecane standard.

Headspace analysis of WSF's. The aqueous WSF solution, 10 mL, was placed in a 30 mL serum bottle containing 4 g NaCl under a nitrogen atmosphere. Immediately, heptane, 0.1 Or 0.5 uL was added as a standard and the bottle sealed. The mixture was shaken vigorously and 50 uL of the

headspace was analyzed by gas chromatography. Each WSF solution was analyzed without addition of the heptane standard also.

Gas chromatography of Gasolines and their WSF's. Separation of the major components of the fuels and their WSF's was achieved on a 1.8 m by 2 mm column of 1.5% OV-101 on 100/120 Chromasorb G/HP programmed from 50 to 150° C at 10°/min on a Varian 2740 gas chromatograph equipped with a flame ionization detector. Components were tentatively identified based on their retention times except as noted below. In one case the saturated components were partially separated by dry column chromatography on a silica gel column 93 x 5.5 mm.

Gas chromatography of Diesel Fuels and their WSF's. Separation of the major components of the fuels and their WSF's was achieved on a 1.8 m by 2 mm column of 1.5% OV-101 on 100/120 Chromasorb G/HP programmed from 100 to 275°C at 8°/min on a Varian 2740 gas chromatograph equipped with a flame ionization detector. Components were tentatively identified based on their retention times.

Gas Chromatography/Mass spectrometry of WSF components. Samples of the WSF of Chevron premium and Shell regular were analyzed by GC/MS. Aliquots of each sample were subjected to a 12 min He purge at 40 mL/min. The volatile components were collected an a sorbent trap and desorbed onto a 1.8 m x 2mm 1% SP-1000 column programmed from 70° to 225°C at 10°/min.

RESULTS

Analysis of Gasolines.

Gas chromatographic analysis of the six gasoline samples indicated the presence of at least 56 individual components. The majority of these components are C_4 to C_{12} hydrocarbons, including benzene, toluene, ethylbenzene, xylenes, and several C_3-benzenes. A typical chromatogram of gasoline is shown in Figure 1. The saturated hydrocarbons (denoted s in Fig. 1) were identified by gas chromatography after partial separation by dry column chromatography on silica gel. Chromatograms of all other gasolines are shown in the appendix figures A1-A5. The estimated amounts of the major monoaromatic hydrocarbons in the gasolines range from 1.8-2.6% benzene, 4.6-18.1% toluene, 8.5-22.5% C_2-benzenes, and 6.5 to 13.0% C_3-benzenes (Table I). All gasolines contained similar amounts of benzene. Generally premiums contained the largest amounts of toluene and the regular gasolines contained the least toluene, C_2-benzenes, and C_3-benzenes. The increased amount of alkylbenzenes in the premium samples probably results from the inclusion of additional product from catalytic reforming (National Research Council, 1981). The agreement between the composition of the gasolines reported herein and that reported previously (Mayrsohn, et al.,1978) is excellent.

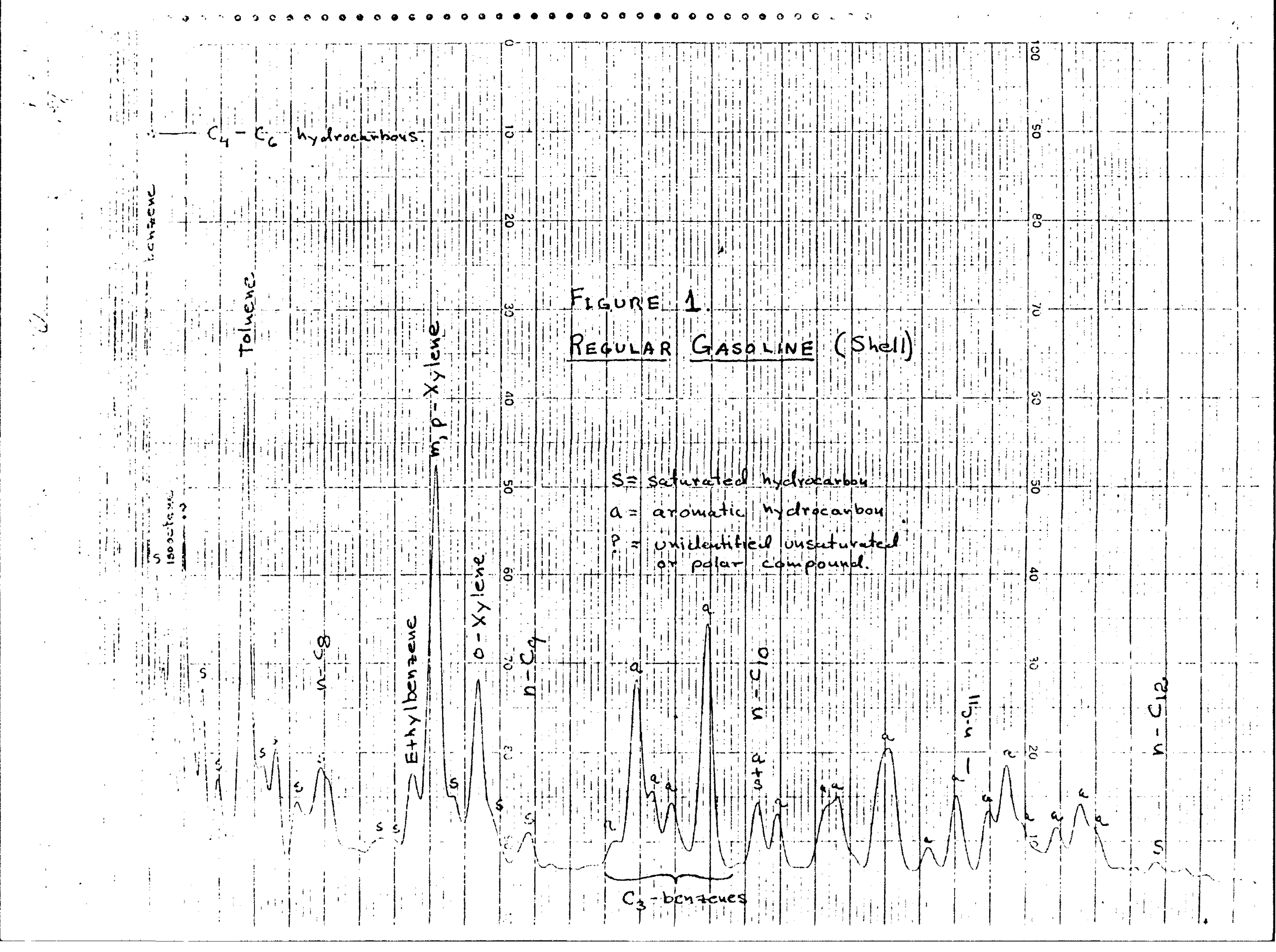
FIGURE 1.
REGULAR GASOLINE (Shell)
S = saturated hydrocarbon
a = aromatic hydrocarbon
? = unidentified unsaturated or polar compound.
$C_4 - C_6$ hydrocarbons.
benzene
isooctane
Toluene
n-C_8
Ethylbenzene
m,p-Xylene
o-Xylene
n-C_9
C_3-benzenes
n-C_{10}
n-C_{11}
n-C_{12}

Table I. Estimation of Aromatic hydrocarbon content of gasolines by gas chromatography[a].

Sample	Benzene %	Toluene %	C_2-Benzenes %	C_3-Benzenes %
Brand A premium	1.8	18.1	22.5	13.0
Brand B premium	2.3	17.2	13.9	9.3
Brand A unleaded	2.5	10.5	13.5	9.7
Brand B unleaded	2.0	6.2	10.6	9.5
Brand A regular	2.1	5.5	8.5	6.5
Brand B regular	2.6	4.6	9.3	8.6
L.A. Composite[b]	1.34	6.73	11.30	9.05

[a]Amounts of aromatic hydrocarbons as % of volatile components were calculated assuming equal flame responses for all components, and the estimates include small amounts of unseparated saturated hydrocarbons. Identifications are based on retention time comparisons. C_2-Benzenes include ethylbenzene and o-,m-,p-xylenes. C_3-benzenes include various methylethylbenzenes, trimethylbenzenes, and propylbenzenes.

[b]Weight % from Mayrsohn _et al._,1978.

The diesel fuels contained a complex mixture of hydrocarbons from C_{10} to C_{18} (Figures A20-A21). The normal alkanes from C_{11} to C_{24} and pristane and phytane are easily visible in the chromatograms of the diesel fuels. The amounts of individual monoaromatics which were less than 0.1% of the total volatile hydrocarbons (Table I) were not detected.

Analysis of WSF's

The chemical composition of the WSF's were determined by both headspace analyis (Table II, Figures A6-A13) and pentane extraction (Table III, Figures A14-A19). The identity of the major components of two of the samples was further substantiated by GC/MS analysis (Table IV). The WSF's contained a mixture of C_4 to C_6 non-aromatic hydrocarbons which are mostly saturated butanes, pentanes and hexanes and several monoaromatics including benzene, toluene and the xylenes. Estimates of the low boiling nonaromatic hydrocarbons range from 25 to 64 mg/L as determined by headspace analysis (Table II.) These estimates are probably low on the basis of comparison to the dynamic headspace analysis data (Table IV.) The best estimates of the levels of aromatic hydrocarbons appear to be the data in Table III because of incomplete extraction in headspace analysis. Benzene values range from 19.1 to 42.5 mg/L, toluene from 17.3 to 61.4 mg/L, and the xylenes from 9.5 to 27.7 mg/L. The WSF's from regular gasolines exhibited the lowest levels of benzene, toluene, and xylenes. The agreement between the pentane extraction technique and the dynamic

headspace analysis is good for benzene and toluene. For comparison with gasoline the composition of the water-soluble fraction determined by headspace analysis is presented as precentages in Table V. The compositions of the WSF's were enriched in benzene, 10 times, and toluene, 2.3 times, compared to the original gasoline.

The WSF's of the diesel fuels are quite different from those of gasoline. The procedures used for the gasolines did not adequately characterize these WSF's. Considerably lower levels of hydrocarbons were observed in water equilibrated with diesel fuel. Further analysis is required for their characterization.

Table II. Chemical Composition of the Water-Soluble Fraction of Gasolines and Diesel Fuels by Static Headspace Analysis.

SAMPLE	$C_4 - C_6$ Non-aromatic Hydrocarbons mg/L	Benzene mg/L	Toluene mg/L	C_2-Benzenes[b] mg/L
Brand A premium	64	44	76	25
Brand A premium[a]	70	35	70	13
Brand B premium	25	17	26	7.8
Brand A unleaded	38	26	32	14
Brand B unleaded	25	12	12	6
Brand A regular	30	14	9	2.5
Brand B regular	42	12	11	4.3
Brand B regular[a]	75	18	20	17
Brand A diesel	0.4	0.03	0.03	-0.005
Brand B diesel	1.2	0.2	0.2	0.1

[a]determined by dynamic headspace analysis (see Table 3).
[b]includes ethylbenzene and xylenes.

Table III. Chemical Composition of the Water-Soluble Fraction of Gasolines by pentane extraction.

SAMPLE	Benzene mg/L	Toluene mg/L	C_2-Benzenes mg/L	Other mg/L
Brand A premium	42	61	28	11
Brand B premium	26	41	17	9.0
Brand A unleaded	42	41	19	10
Brand B unleaded	28	25	14	9.4
Brand A regular	25	20	9.5	5.7
Brand B regular	19	17	11	12

Table IV. Gas chromatography/ mass spectrometry identification of Volatile components of the WSF's of representative gasolines.

	Concentration (mg/L)					
Sample	C_4-HC	C_5-HC	Benzene	Toluene	Xylenes	Ethylbenzenes
Brand A premium	45	25	35	70	10	2.8
Brand B regular	30	45	18	20	16	0.6

C_4-HC and C_5-HC are hydrocarbons containing 4 and 5 carbon atoms,resp.

Table V. Estimation of Aromatic hydrocarbon content of the WSF's of gasolines by head space gas chromatography[a].

Sample	Benzene %	Toluene %	C_2-Benzenes %	C_3-Benzenes %
Brand A premium	21.5	38.5	11.6	2.0
Brand B premium	22.5	32.7	11.9	3.4
Brand A unleaded	25.3	28.1	10.8	2.6
Brand B unleaded	24.0	21.0	11.4	2.1
Brand A regular	25.8	17.4	7.3	0.8
Brand B regular	17.1	15.4	5.9	3.1

[a]Amounts of aromatic hydrocarbons as % of volatile components were calculated assuming equal flame responses for all components. Identifications are based on retention time comparisons. C_2-Benzenes include ethylbenzene and o-,m-,p-xylenes. C_3-benzenes include various methylethylbenzenes, trimethylbenzenes, and propylbenzenes.

Determination of Diffusion constants.

Molecules of gasoline components diffuse fron the gasoline-water interface in solution according to Fick's First Law of Diffusion:

$$dm/dt = -DA(\ C/\ X)_{y,z}$$

Where

D = diffusion coefficient
m = mass of substance
A = area of interface
t = time
X = distance
C = concentration

Then the approximation, $((C-C_s)/X) = (\ C/\ X)_{y,z}$ can be substituted for the concentration gradient with

C = concentration in solution
C_s = concentration at interface
X = distance at which C is measured.

Then $$dm/dt = -DA(C-C_s)/X$$

For a container of volume V, the above equation becomes:

$$dc/dt = -DA(C-C_s)/XV$$

Integration yields:

$$C = (C_s - C_s)\exp(-DAt/XV)$$

assuming C_s = C at equilibrium or C_e, then

$$(C_e - C)/C_e = \exp(-DAt/XV)$$

A plot of $\ln[(C_e-C)/C_e]$ versus t should give a straight line whose slope, $m = -DA/XV$, and the diffusion constant $D = -mXV/A$. In our experiments, the absorbances of the WSF's being proportional to the concentrations were used in the regressions.

For our experimental container X = 14.9 cm, A = 110.8 cm^2 and V = 1890 cm^3 giving XV/A = 254 cm^2 (.0254 m^3) so that D = -254 cm^2 times the slope of the plot of $\ln[(C_e-C)/C_e$ versus t. The slopes of the regression lines and the dispersion constants are presented in Table VI.

The absorbance of the WSF's increased with time as shown in Figure 2. For the regression, an extrapolated final absorbance was used. This value was frequently lower than the absorbance at 2000 hr and similar to that of the stirred preparation. The higher value at 2000 hr is probably due to some oxidation of components of the WSF.

The time required for 95% saturation ($t_{95\%}$) of a quiescent body of water with gasoline can be estimated from

$$t_{95\%} = -2.996\ XV/DA$$

X = distance from interface to bottom of water in cm
V = volume of water in cm^3
A = interfacial area in cm^2
D = diffusion constant in cm^2/hr

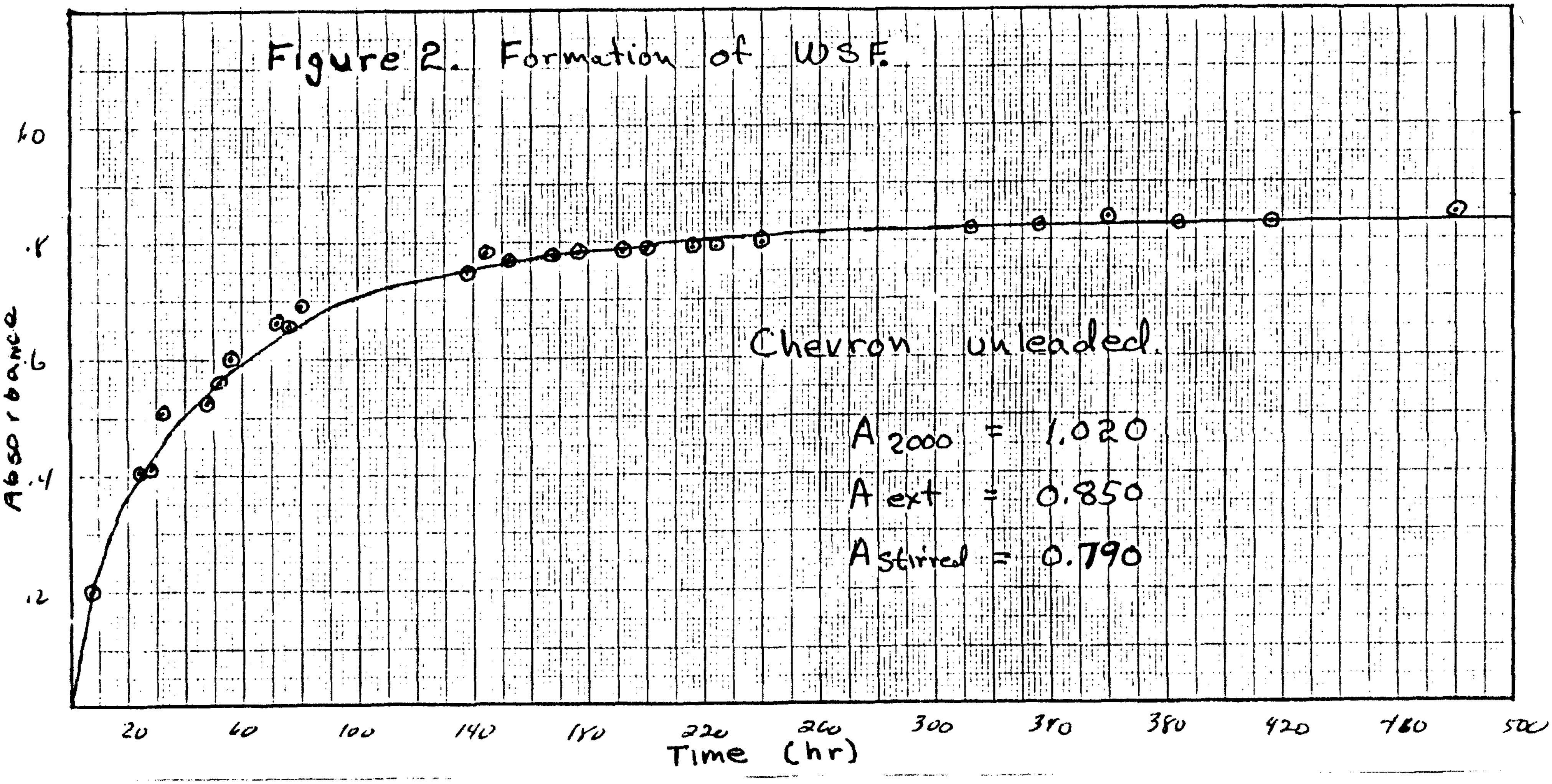

Figure 2. Formation of WSF.
Chevron unleaded.
A 2000 = 1.020
A ext = 0.850
A stirred = 0.790
Absorbance
1.0
.8
.6
.4
.2
20
60
100
140
180
220
260
300
340
380
420
460
500
Time (hr)

Table VI. Diffusion constant data for formation of WSF's under static conditions at 18°C.

Sample	Slope	r	D	n	$t_{1/2}$	A	
Chevron premium	-0.0062	0.997	1.6	24	111	0.70	260
Chevron unleaded	-0.015	0.984	3.8	16	45	0.88	272
Chevron regular	-0.021	0.988	5.3	16	34	0.66	272
Shell premium	-0.0046	0.993	1.2	24	151	0.85	260
Shell unleaded	-0.021	0.998	5.3	15	32	1.70	272
Shell regular	-0.023	0.994	5.8	16	30	2.00	272
Shell diesel	-0.0083	0.994	2.1	8	83	0.44	262
Chevron diesel	-0.012	0.993	3.0	8	55	1.05	259

Slope is the slope of the regression of $\ln[(A_e - A_t)/A_e$ on t
r is the product moment correlation coefficient
D is the diffusion constant in cm^2/hr
n is the number of data points
$t_{1/2}$ is the half life in hr for saturation in static conditions used.
A_e is extrapolated equilibrium absorbance at .

Ultraviolet Spectroscopy of the WSF's.

In the determination of the diffusion constants the UV spectra of the WSF's were recorded from 350 to 240 nm. All WSF's exhibited an intense absorption below 250 nm which tailed to higher wavelengths. In the region from 300-250 nm the spectra of the WSF's contained surprisingly different features which are summerized below.

Chevron premium	multiplet @ 248,254,261,268 nm
Shell premium	shoulder @ 268 nm
Chevron unleaded	shoulders @ 253,260,268 nm
Shell unleaded	doublet @ 272,277 nm
Chevron regular	shoulder @ 243 nm multiplet @ 260,268,272,276 nm

Shell regular	doublet @ 272, 276 nm
Chevron diesel	no peaks or shoulders tail to 350 nm
Shell diesel	broad peak centered @ 270 nm

Each WSF exhibits a characteristic and distinguishable pattern of peaks and shoulders with the single exception of the Shell regular whose spectrum is qualitatively the same as the Shell unleaded. This finding suggests that the UV spectra of the WSF's can be used in the identification of gasolines in conjunction with the determination of lead content.

DISCUSSION

Gasolines contain a complex mixture of hydrocarbons both saturated and aromatic. The monoaromatic hydrocarbons including benzene and the alkylbenzenes represent a major portion of the gasolines studied. This result agrees with analyses summarized by the National Research Council (National Research Council, 1981) Table VII.

Table VII. Alkylbenzene composition of a Composite Gasoline obtained in the Los Angeles Area*.

Compound	Wt %	Compound	Wt %
Benzene	1.34	Isobutylbenzene	0.08
Toluene	6.73	<u>sec</u>-butylbenzene	0.09
Ethylbenzene	1.71	<u>tert</u>-butylbenzene	0.12
<u>m</u>- and <u>p</u>-Xylene	6.73	1-Methyl-3-propylbenzene	0.56
<u>o</u>-Xylene	2.86	1-Methyl-4-isopropylbenzene	0.02
Isopropylbenzene	0.14	1-Methyl-2-<u>N</u>-propylbenzene	0.15
Propylbenzene	0.61	1,2-Diethylbenzene	0.57
2-Ethyltoluene	0.96	1,3-Diethylbenzene	0.08
3- and 4-Ethyltoluene	2.89	1,3-Dimethyl-2-ethylbenzene	0.59
1,2,4-Trimethylbenzene	3.30	1,2,4,5-Tetramethylbenzene	0.37
1,3,5-Trimethylbenzene	1.15	1,2,3,5-Tetramethylbenzene	0.15
Butylbenzene	0.44	Naphthalene	0.46
		Total	32.10 (a)
		Total Saturates	65

* From Mayrsohn et al., 1978.

(a) Unidentified alkyl benzenes would probably raise this figure to approximately 35%.

When gasoline contacts water several processes occur. The gasoline may become emulsified or dispersed in the water. The more soluble components may dissolve forming what is referred to as the water soluble fraction (WSF). The more volatile components may evaporate. In a spill situation where the gasoline is in contact with both air and water evaporation will exceed dissolution as a result of the more rapid mass transfer to the vapor phase. In addition, in this case, the evaporation of the WSF, as described by Henry's Law, is rapid; therefore little accumulation of gasoline components is expected. However, in a spill situation underground, where the gasoline is mostly in contact with water, considerable transfer of the components of the WSF may occur. The potential for groundwater contamination by underground spills has received less attention in the literature but may be equally important.

The WSF's of the gasolines analyzed were enriched considerably in total aromatic hydrocarbons and especially in benzene and toluene. A body of water in equilibrium with gasoline (9:1) may contain benzene levels as high as 40 mg/L and toluene levels from 9 to 76 mg/L based on the laboratory equilibrations (Table II-III). The differences in determination of the aromatic hydrocarbons by headspace analysis and pentane extraction are minor and result from differences in extraction efficiency.

The actual concentrations obtained in an environmental situation depend of a variety of factors. The laboratory derived equilibrium values represent a maximum obtainable concentration. These equilibrium values exceed the EPA ambient water quality values (U.S. Environmental Protection Agency, 1979a, 1979b, 1981) for benzene and toluene:

	24-hr avg.	Max. Limit	Environment
benzene	3.100 mg/L	7.000 mg/L	Freshwater
	0.920 mg/L	2.100 mg/L	Saltwater
		0	Human Health
toluene	2.300 mg/L	5.200 mg/L	Freshwater
	0.100 mg/L	0.230 mg/L	Saltwater
		12.4 mg/L	Human Health
ethylbenzene		1.1 mg/L	Human Health

Unless the criterion for benzene is relaxed, gasoline comtamination of water will result in a level of benzene greater than the zero value for the human health criterion. In extreme situations the criteria for aquatic life may be exceeded also.

Reviews of the effects of benzene, toluene, ethylbenzene, and the alkylbenzenes are available (U.S.Environmental Protection Agency, 1979a, 1979b,1981). The criteria above reflect these data. However, virtually no attention has been paid to the C_4 to C_6 hydrocarbons. Their toxicity is not known at present. One study (Hutchinson, et al.,1979) with the marine algae, *Chlorella vulgaris* and *Chlamydomonas angulosa*, suggests that the toxicity of hydrocarbons is a function of their solubility in water (Table VIII). Hexane was found to be about 10 times more toxic than benzene. If this phenomenon is general, then the saturated hydrocarbons will exhibit toxicities to aquatic life greater than toluene and benzene (compare solubilities Table VIII.). The toxicity of the WSF's of gasoline may be the result in large part from the toxicity of saturated compounds in the WSF's. and will require further study for adequate assessment.

Table VIII. Solubilities of Hydrocarbon constituents of the water soluble fraction of gasolines (McAuliffe,1966).

Compound	Solubility mg/L	Compound	Solubility mg/L
Butane	61.4	Benzene	1780
Isobutane	48.9	Toluene	515
Pentane	38.5	o-Xylene	175
Isopentane	47.8	Ethylbenzene	152
2,2-dimethylpropane	33.2	1,2,4-Trimethylbenzene	57
Hexane	9.5		
2-methylpentane	13.8		
3-Methylpentane	12.8		
2,2-dimethylbutane	18.4		

The dispersion constants (Table IV) indicate that dissolution in a quiescent situation is rather slow. The half-life for saturation of a 15 cm deep water layer varied from 30 to 151 hr. The reason for the variation in diffusion constant from 1.2 to 5.8 cm^2/hr is unknown. It may result from effect of various additives.

The characterization of the WSF's herein focused on the major soluble and volatile components as determined by gas chromatography. The characterization of additives of low volatility and high aqueous solubility, i.e. those not extracted by pentane, was not attempted.

Monoaromatic hydrocarbons, including benzene, toluene, and the xylenes, constitute an important fraction of gasoline (23-55%) anJ the major components of the water soluble fraction (42-74%). Benzene, which is enriched by a factor of ten in the water soluble fraction, is important as an environmental comtaminant because of its link to leukemia. Under conditions where evaporation is suppressed, benzene and the alkyl aromatic hydrocarbons may pose a threat to aquatic life. The importance of the C_4 to C_6 saturated hydrocarbons cannot be assessed; however, these compounds may exhibit considerable toxicity to aquatic organisms.

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APPENDIX of CHROMATOGRAMS

Figure legends.

Fig. A1

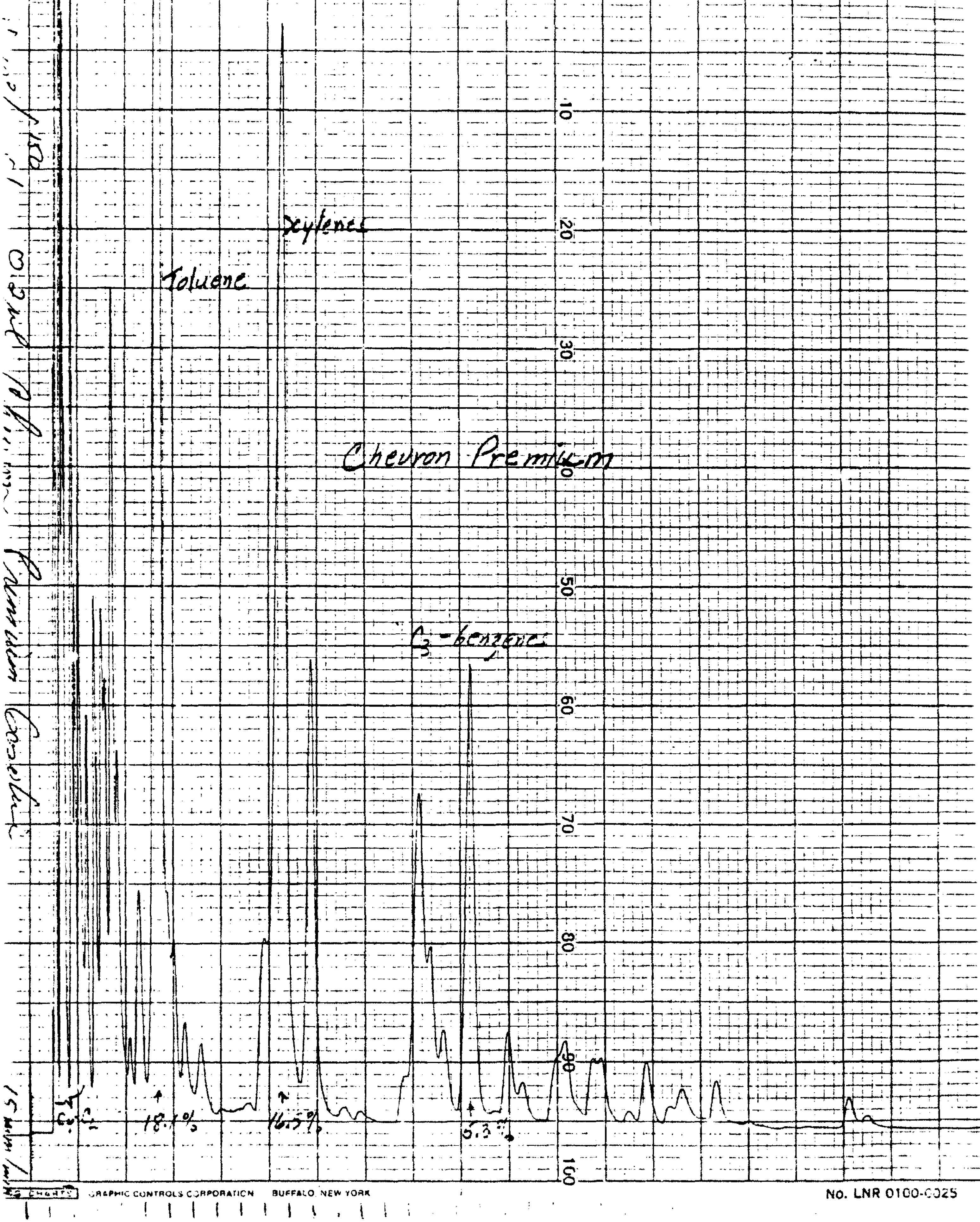
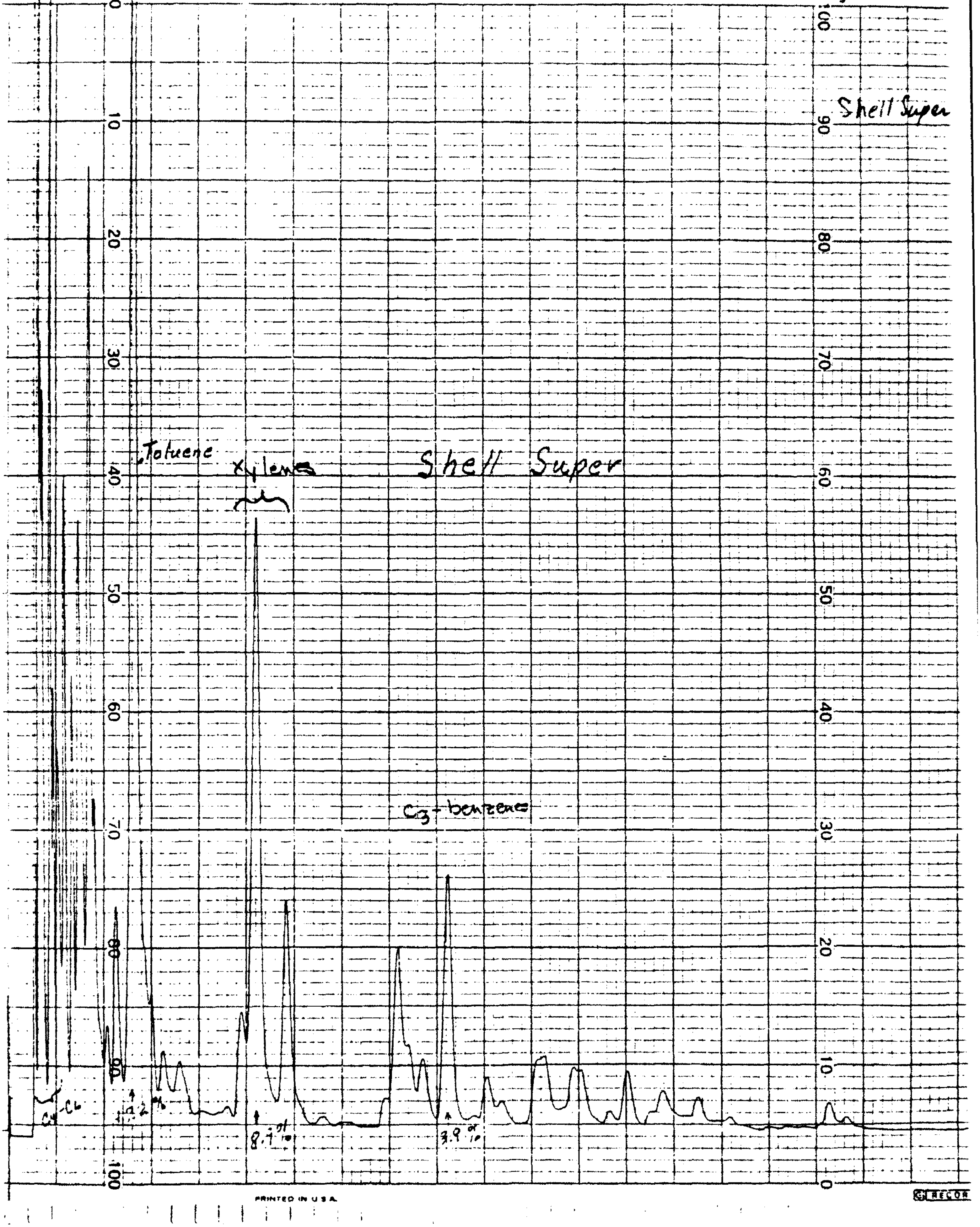

Toluene
Xylenes
Chevron Premium
C_3-benzenes
18.1%
16.5%
5.3%
0
10
20
30
50
60
70
80
90
100
GRAPHIC CONTROLS CORPORATION BUFFALO, NEW YORK
No. LNR 0100-0025

Fig A2



Shell Super
Toluene
xylenes
Shell Super
C3-benzene
C4
C6
PRINTED IN U.S.A.

Fig. A3

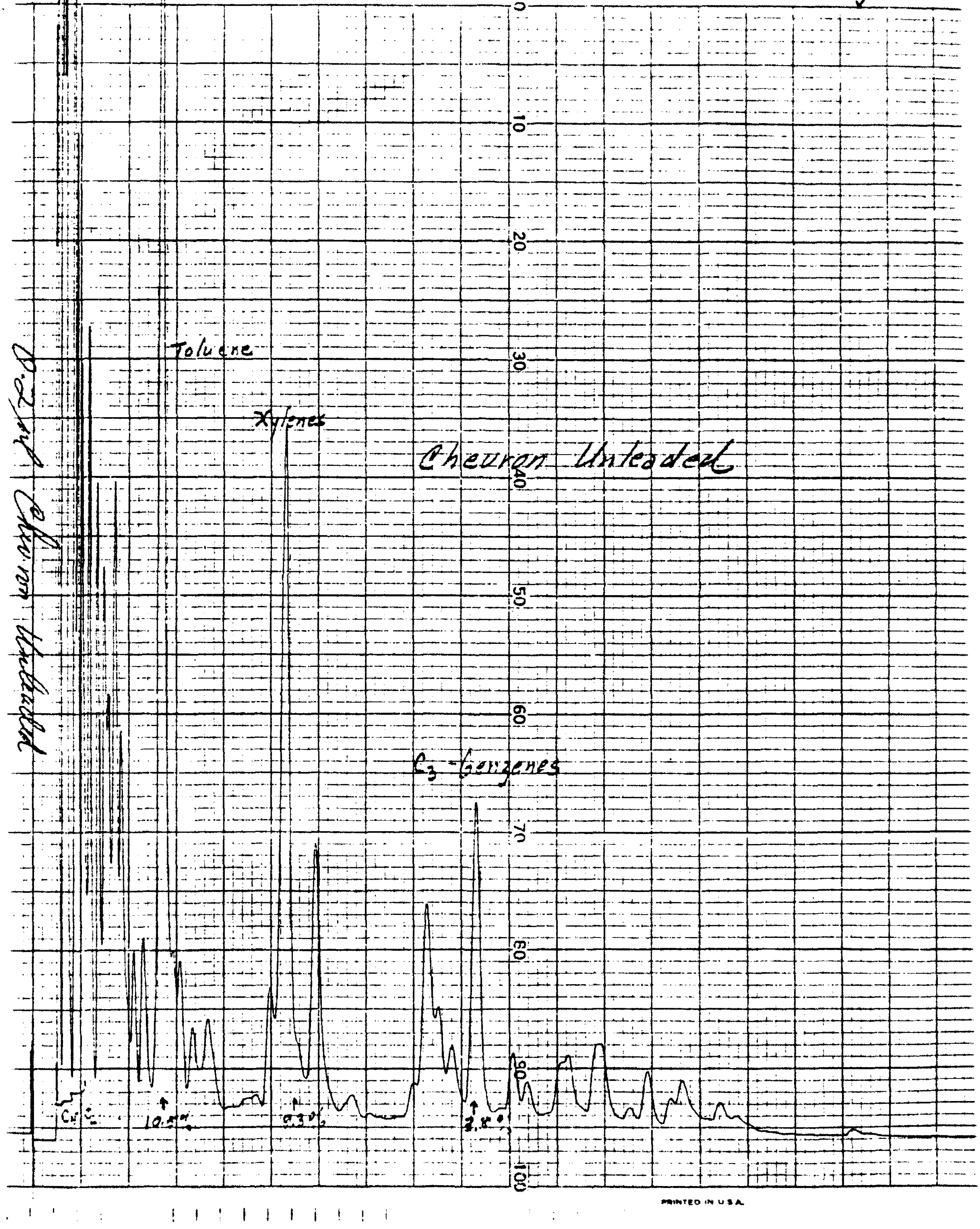

Toluene
Xylenes
Chevron Unleaded
C_3-Benzenes
0
10
20
30
40
50
60
70
80
90
100
PRINTED IN U.S.A.

Fig. A4

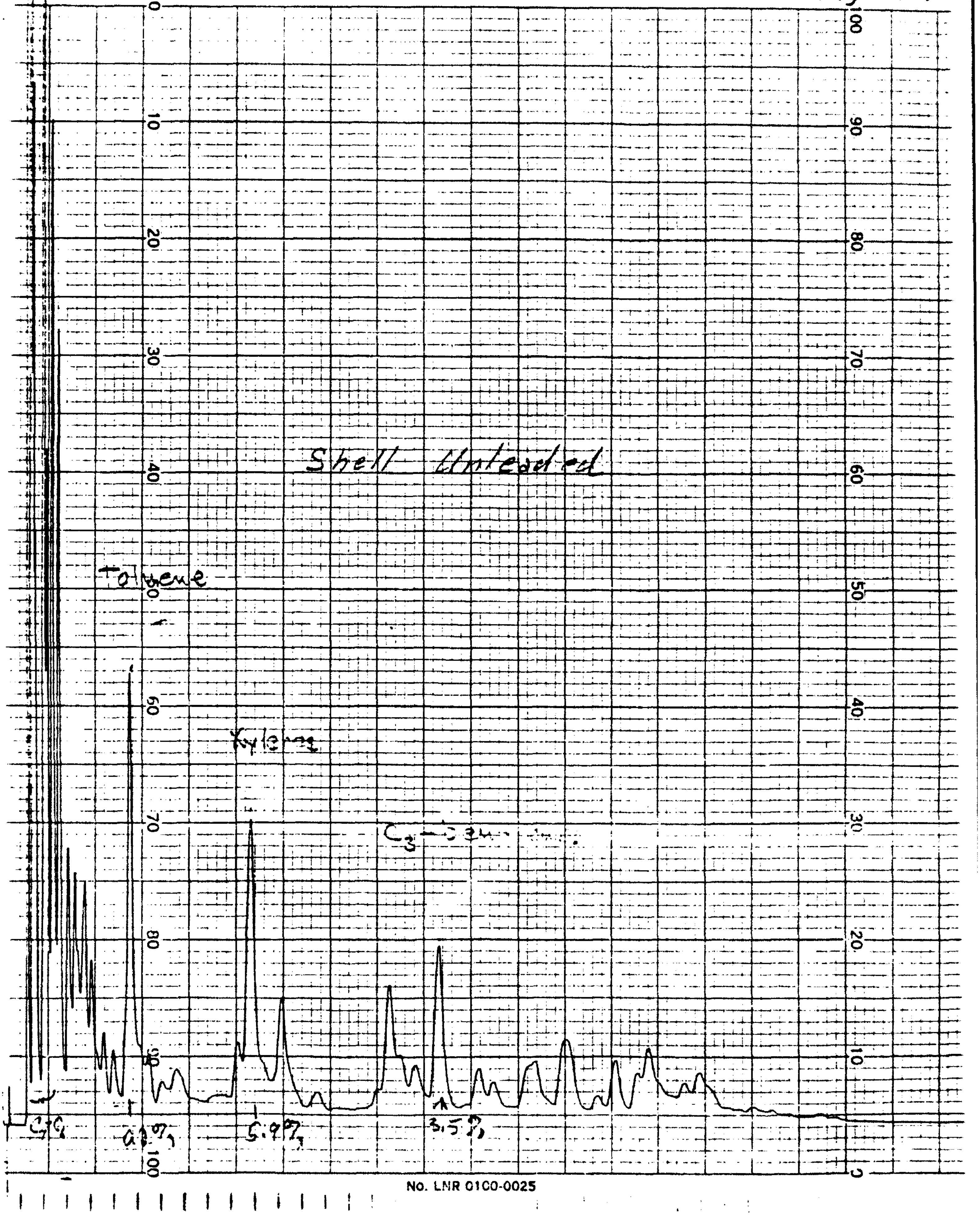
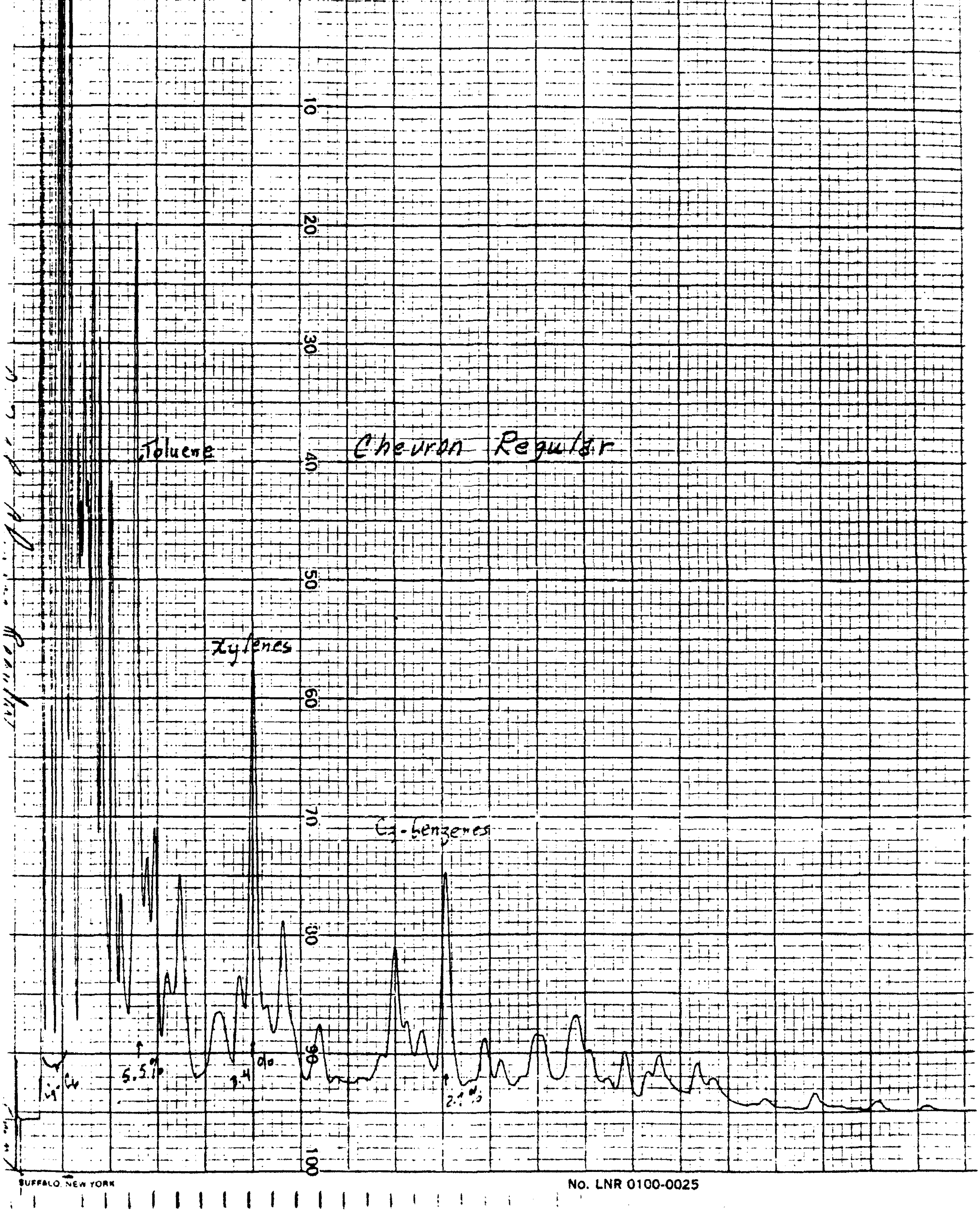
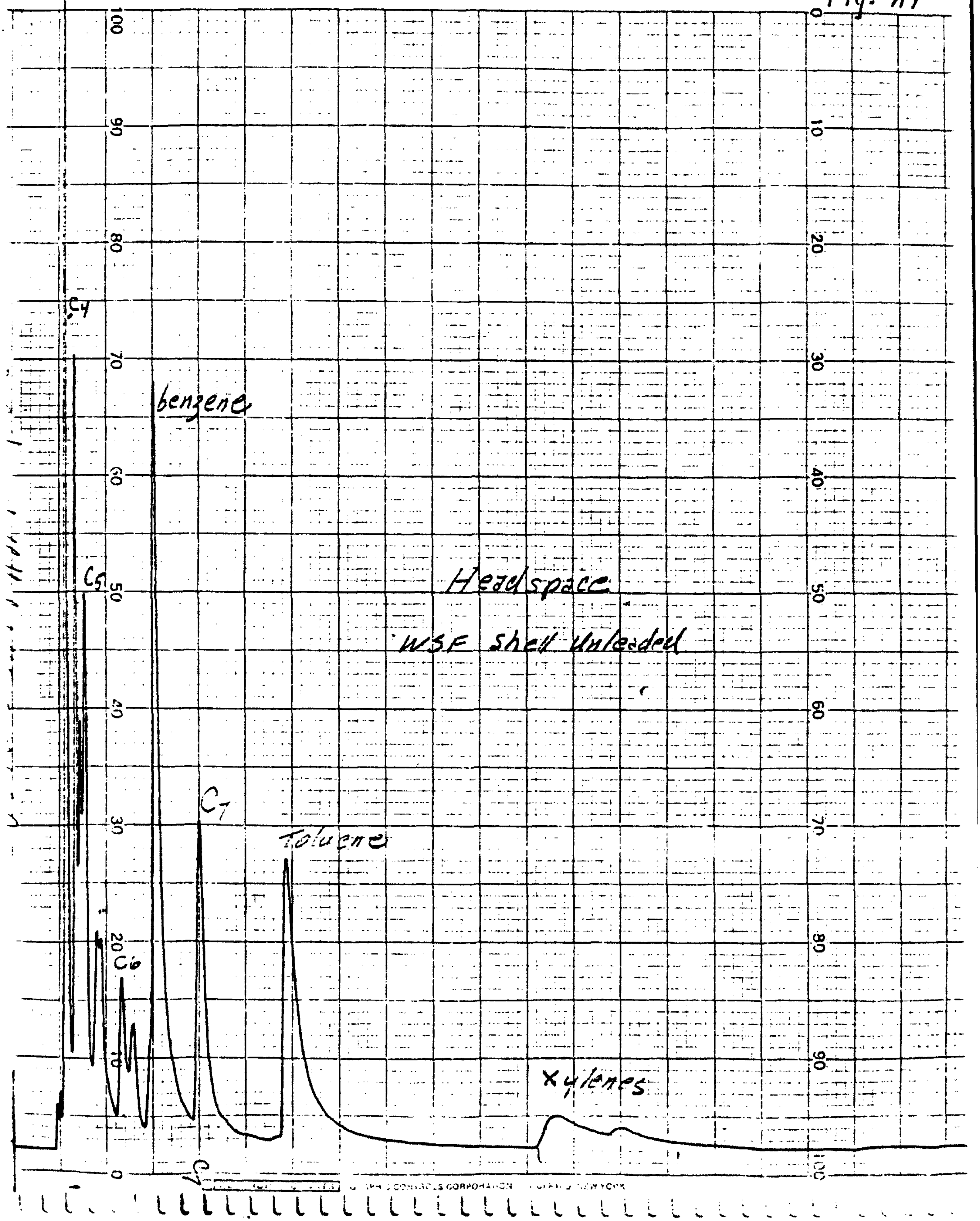


Fig. A5



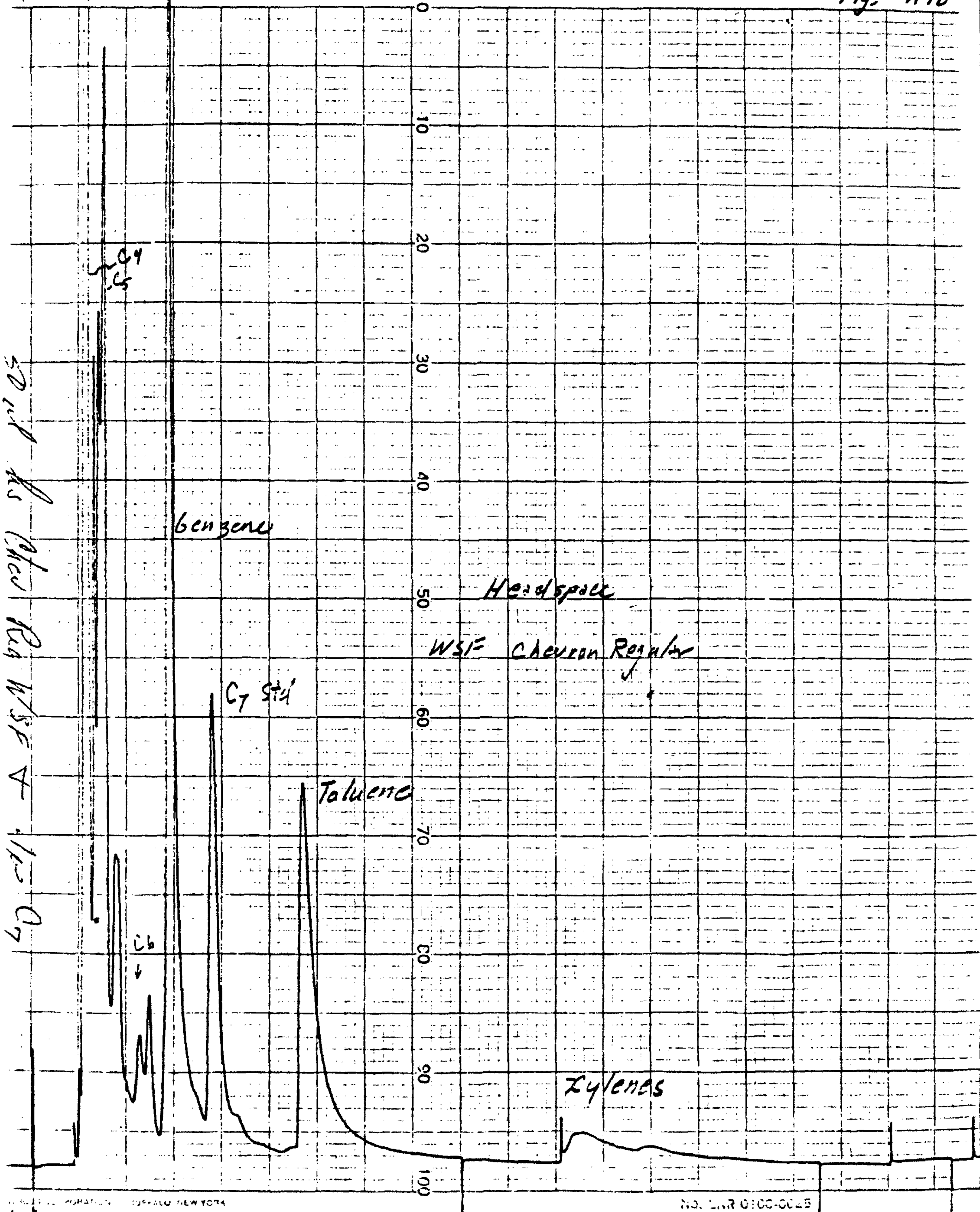
0
10
20
30
40
50
60
70
80
90
100
Toluene
Chevron Regular
Xylenes
C3-benzenes
5.5%
9.4
2.1%
BUFFALO, NEW YORK
No. LNR 0100-0025

Fig. A9



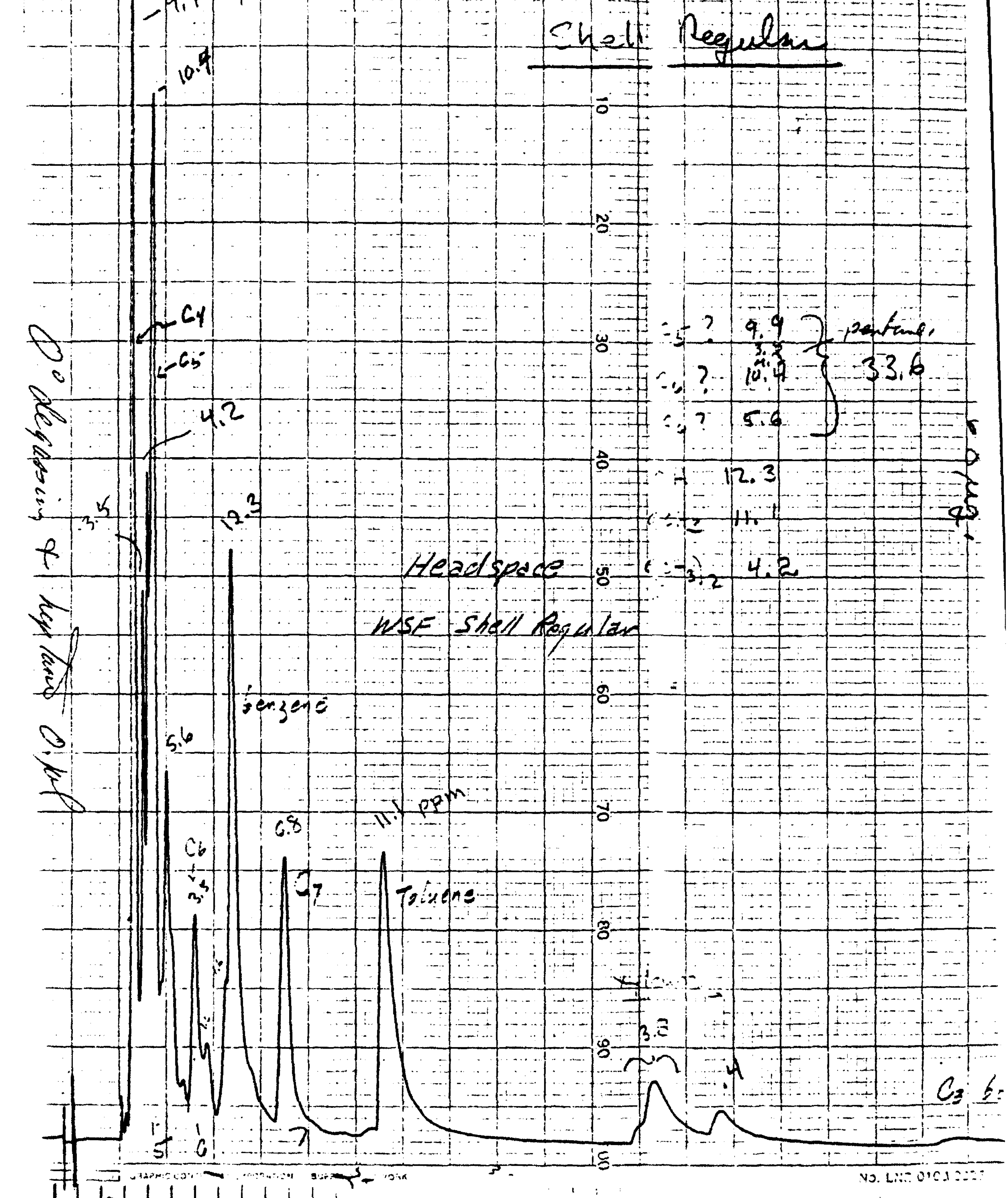
C4
C5
C6
benzene
C7
Toluene
Xylenes
Headspace
WSF Shell Unleaded

Fig. A10



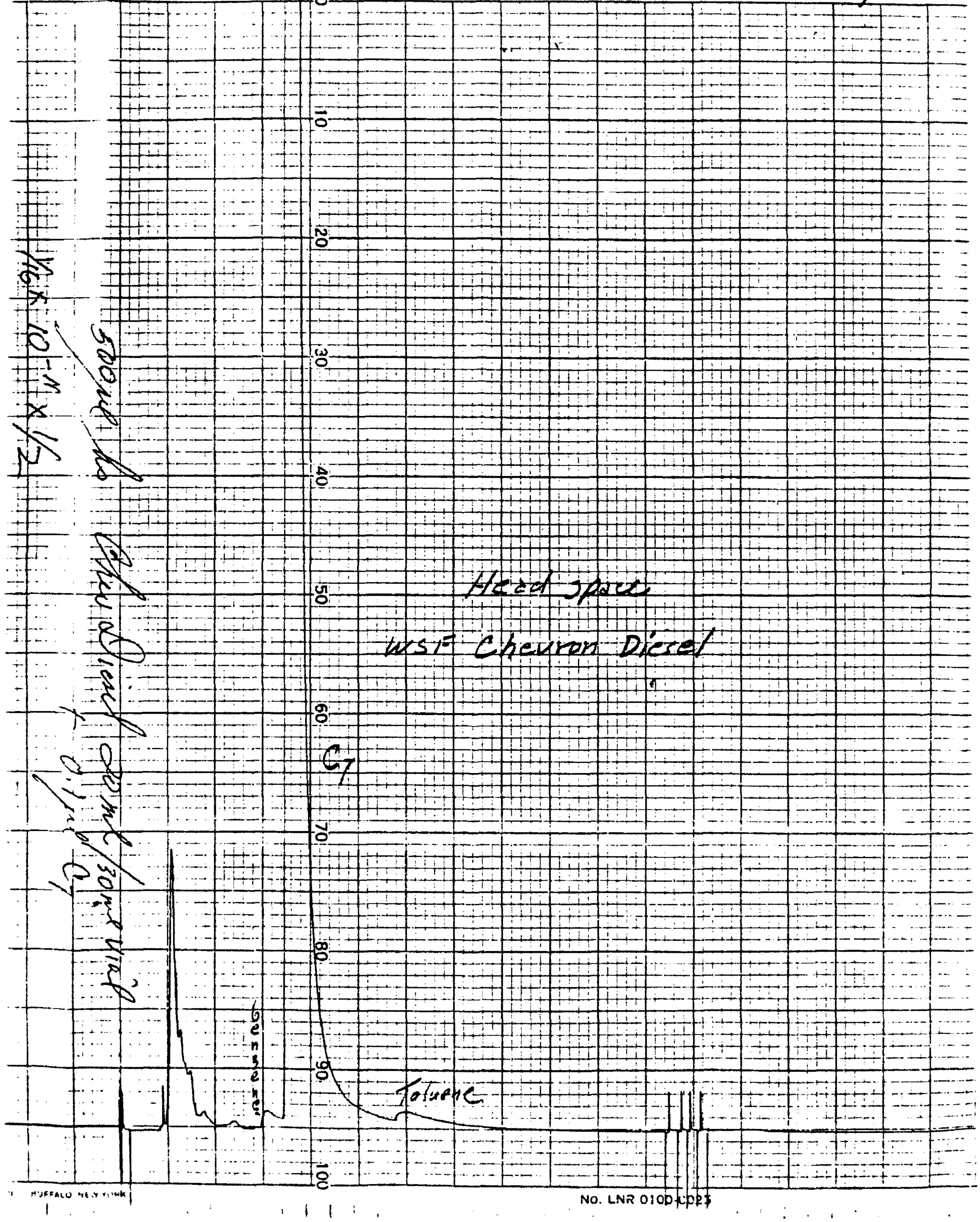
C_4
C_5
Benzene
C_7 Std
Toluene
C_6
Headspace
WSF Chevron Regular
Xylenes
0
10
20
30
40
50
60
70
80
90
100
BUFFALO NEW YORK
NO. LKR 0100-0025

Fig. A11



Shell Regular
Headspace
WSF Shell Regular
benzene
Toluene
11.1 ppm
9.9
10.4
4.2
5.6
12.3
6.8
3.5
C4
C5
C6
C7
pentane
33.6

Fig. A12


Head space
WSF Chevron Diesel
Toluene
C7
0
10
20
30
40
50
60
70
80
90
100
BUFFALO NEW YORK
NO. LNR 0100-C023

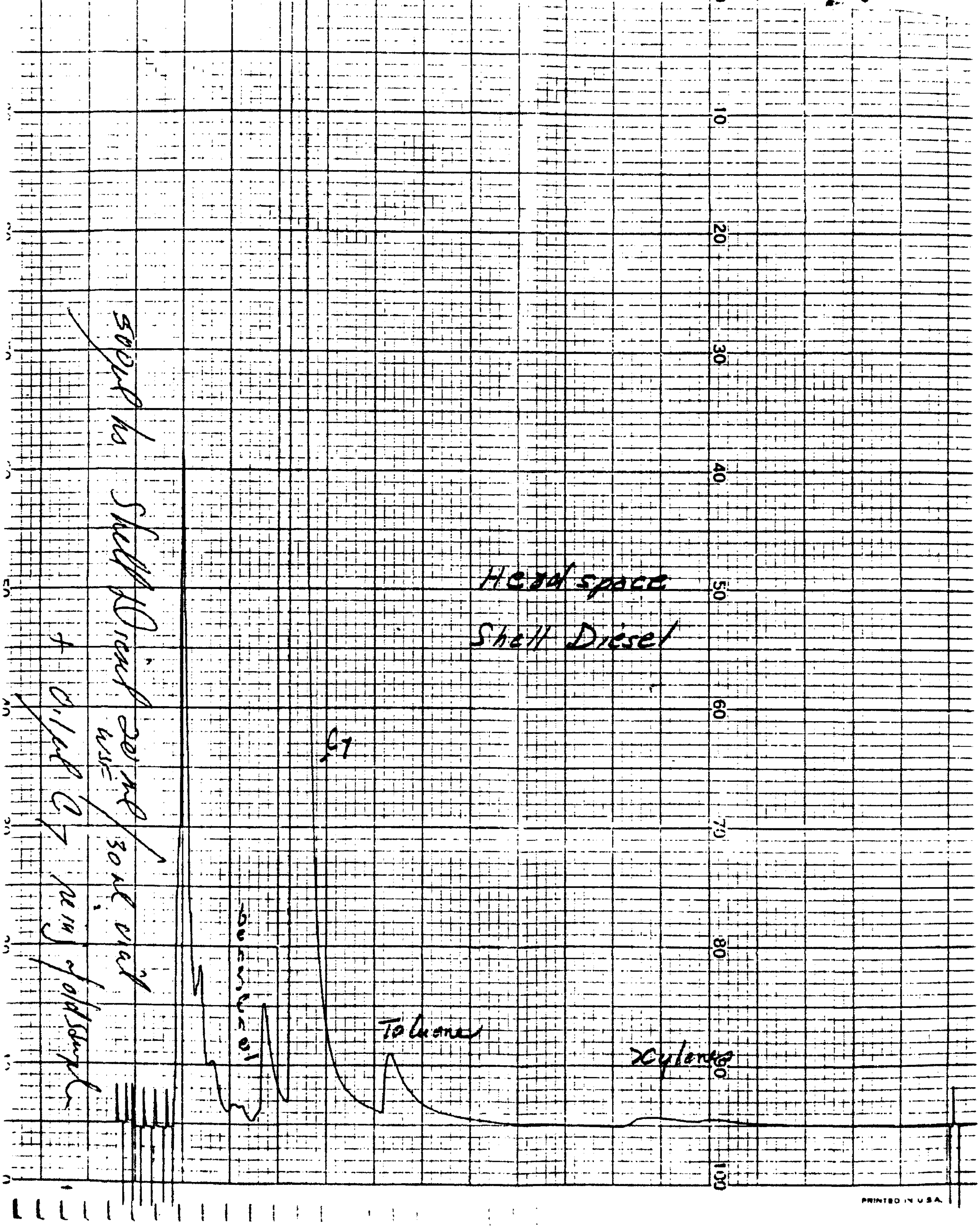
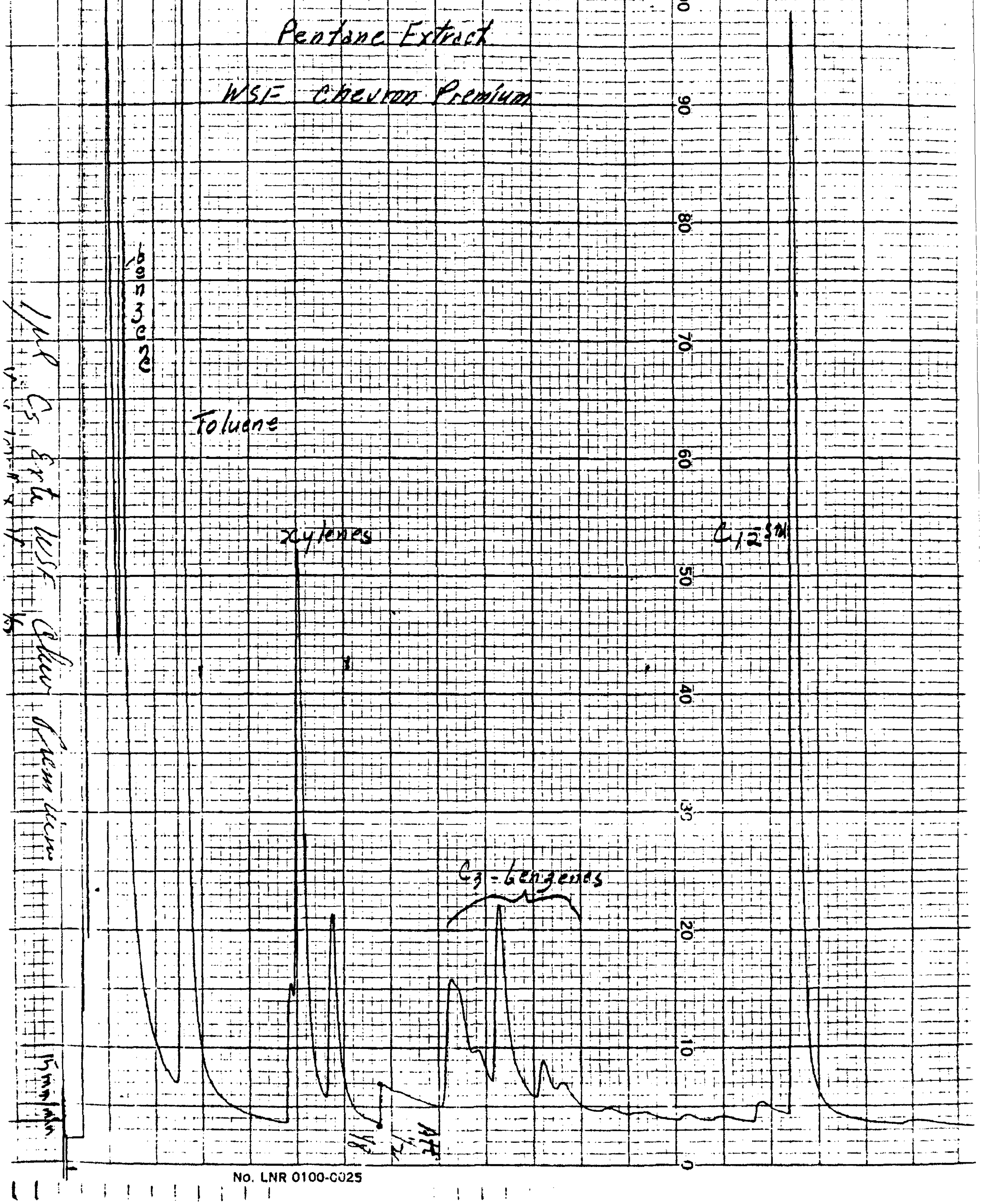

0
10
20
30
40
50
60
70
80
90
100
Head space
Shell Diesel
C7
Toluene
Xylenes

Fig. A13

Fig. A14.


Pentane Extract
WSF Chevron Premium
benzene
Toluene
xylenes
C3-benzenes
C12 Std
1/8
1/2
AT
1 µl C5 Extr WSF Chev Premium
15mm/min
100
90
80
70
60
50
40
30
20
10
0
No. LNR 0100-0025

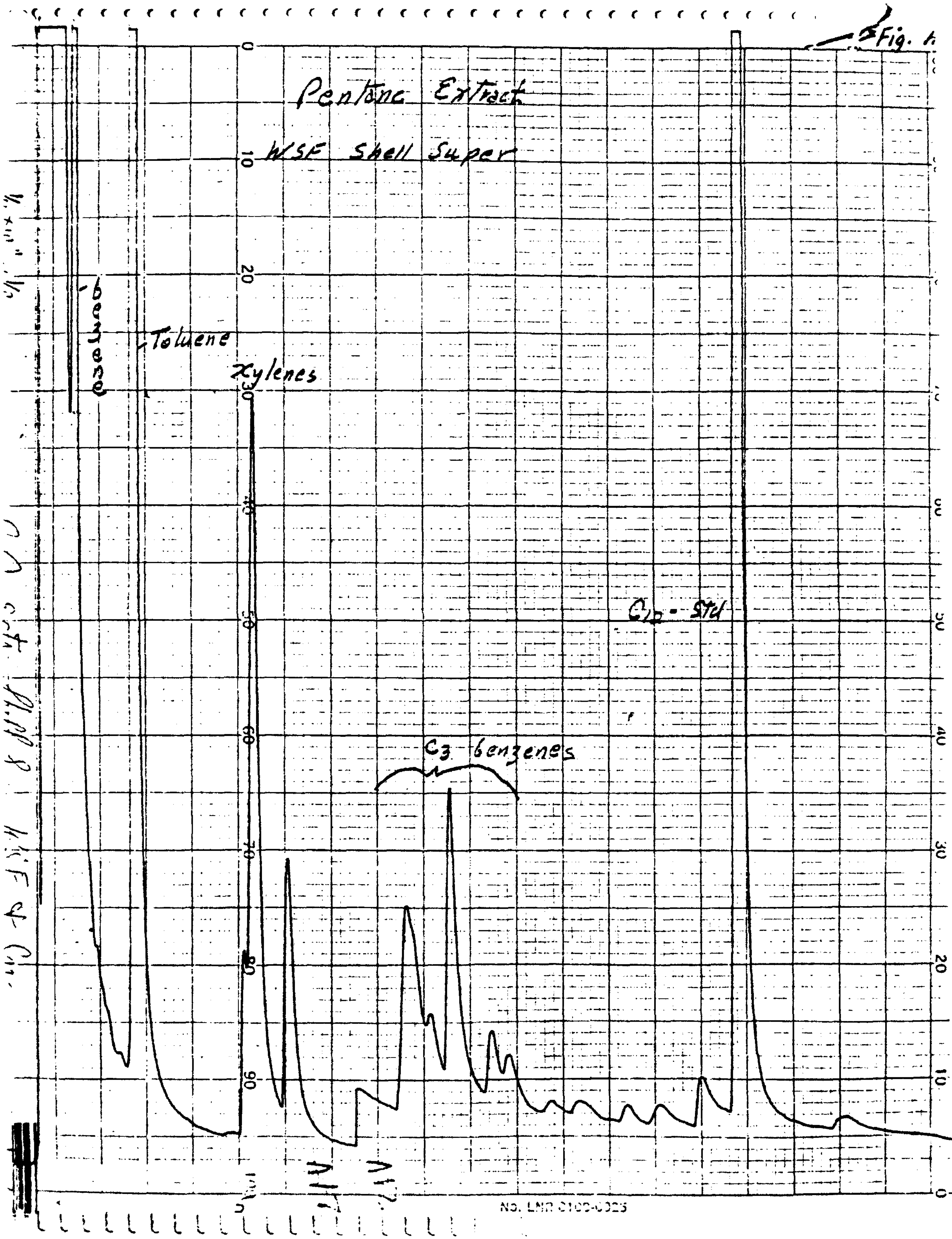
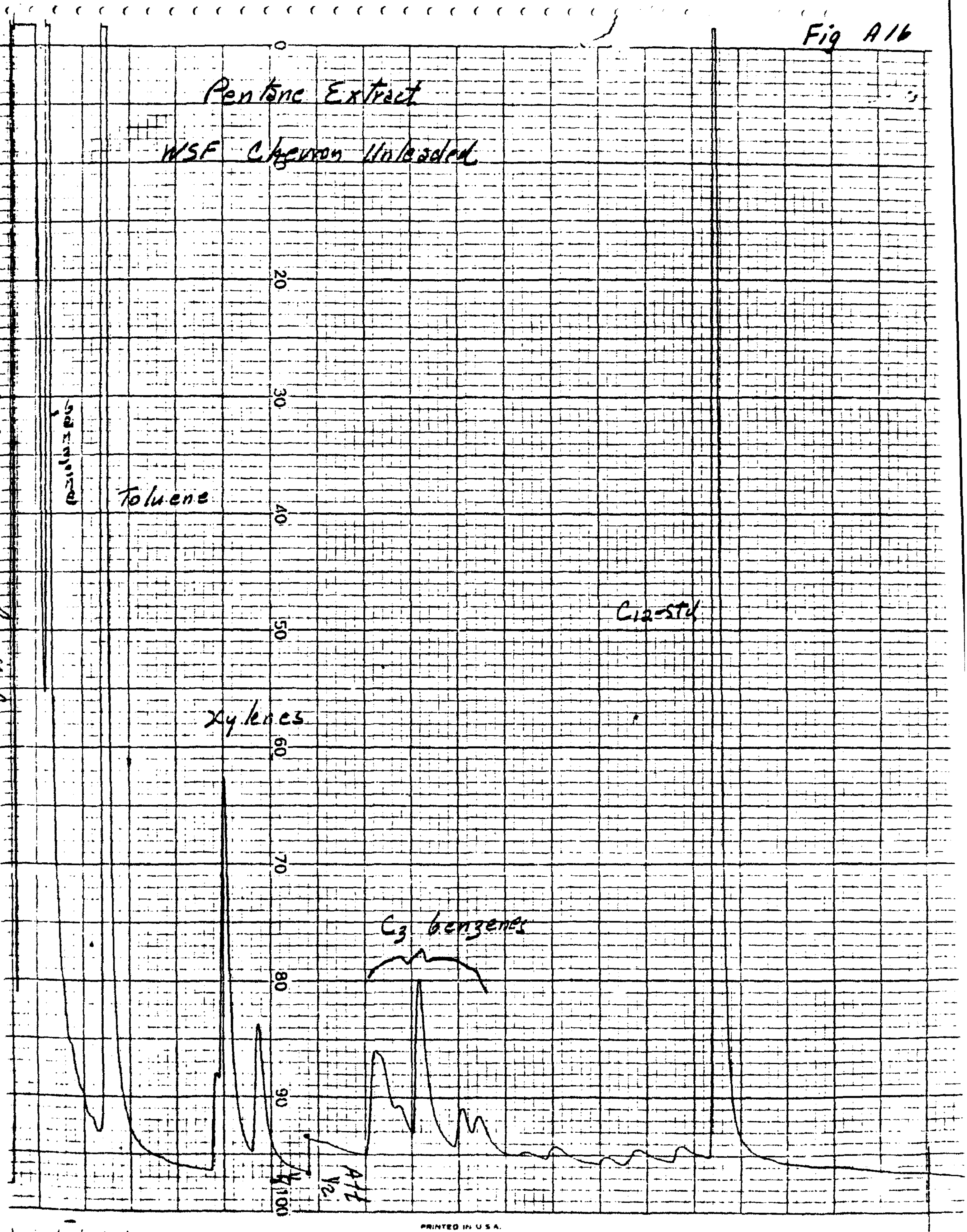


Fig. A
Pentane Extract
WSF Shell Super
benzene
Toluene
xylenes
C_3 benzenes
C_{12} - Std

Fig A16



Pentane Extract
WSF Chevron Unleaded
Benzene
Toluene
Xylenes
C3 benzenes
C12-std
Att 1/2
0
20
30
40
50
60
70
80
90
100
PRINTED IN U.S.A.

Fig A6

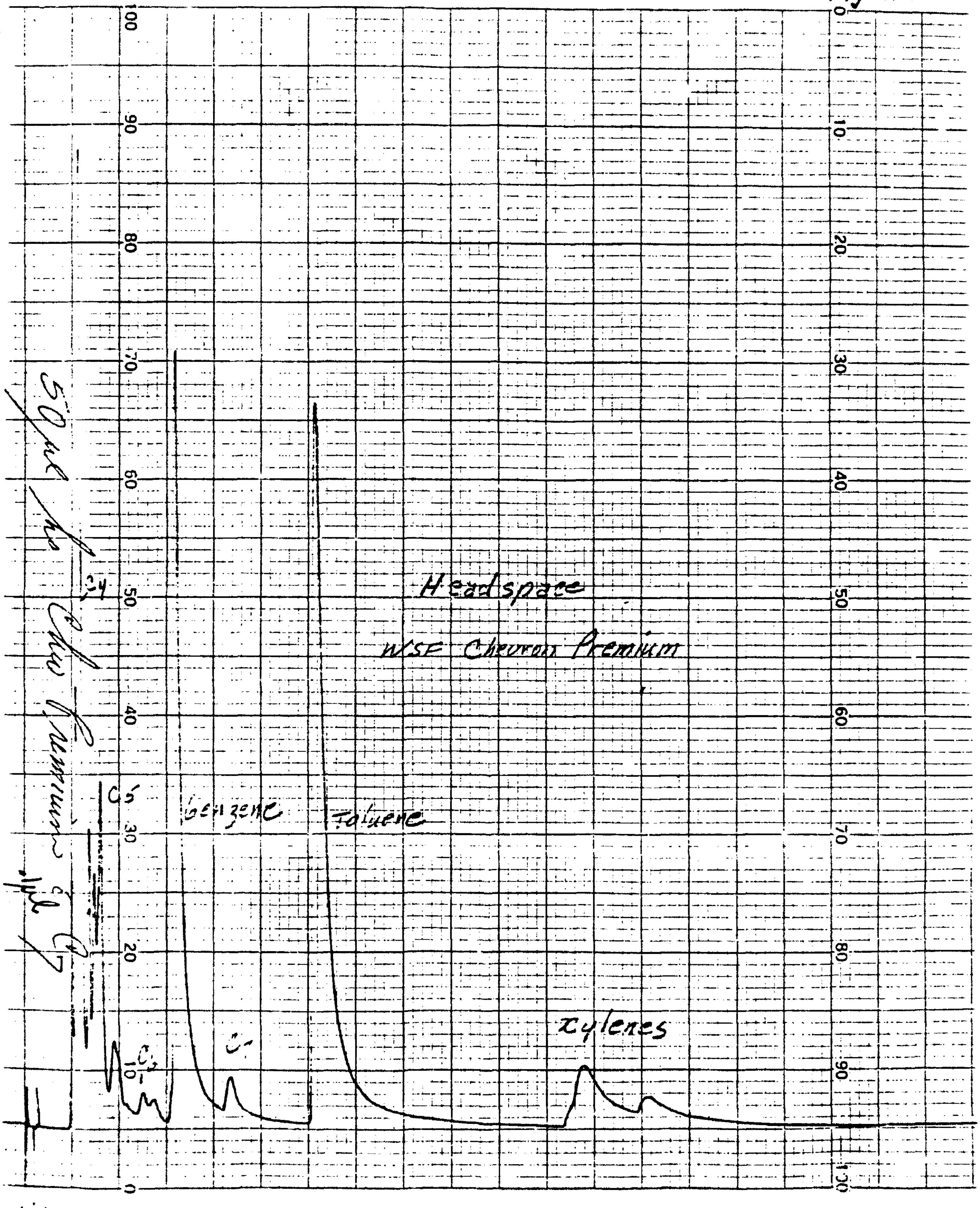
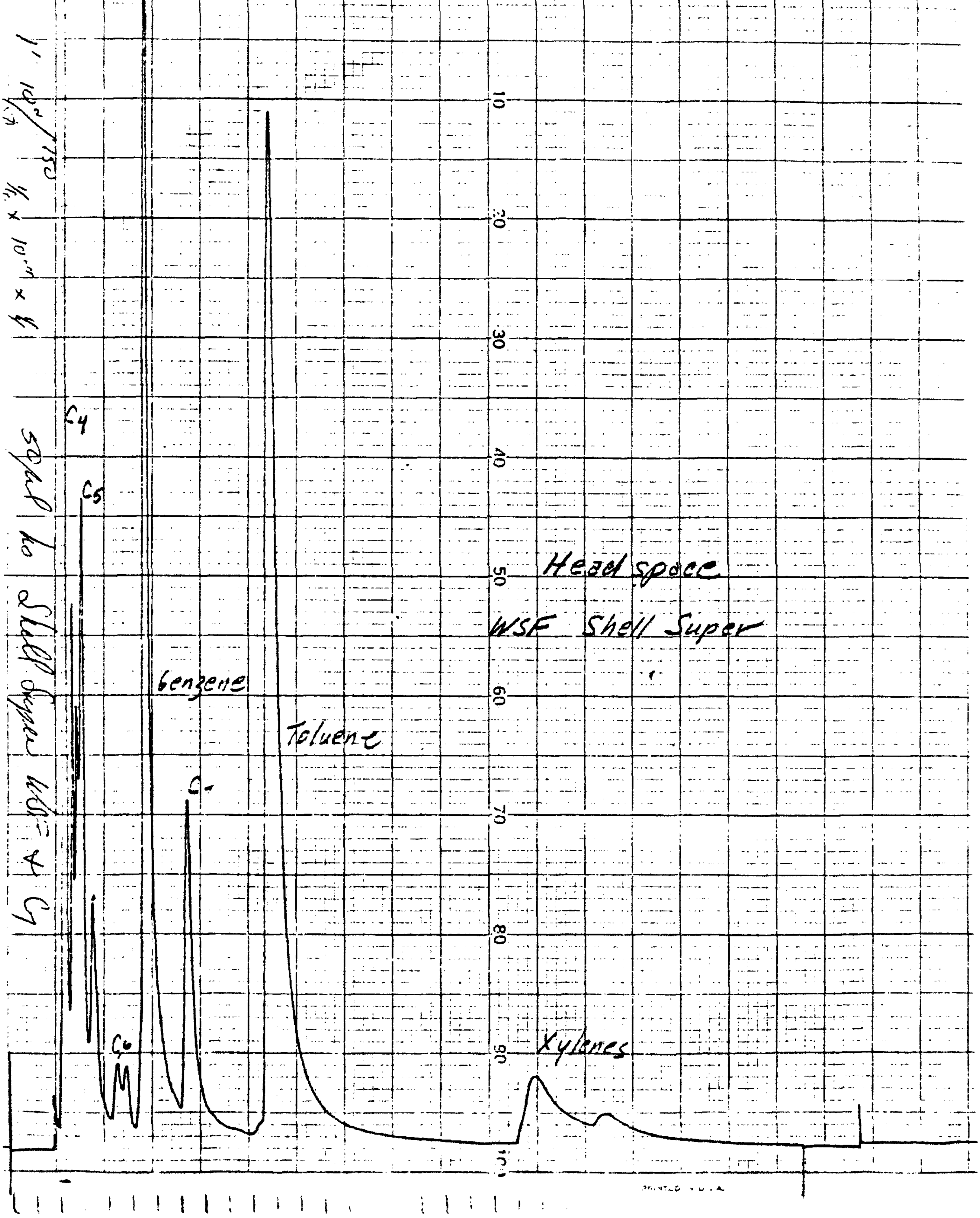
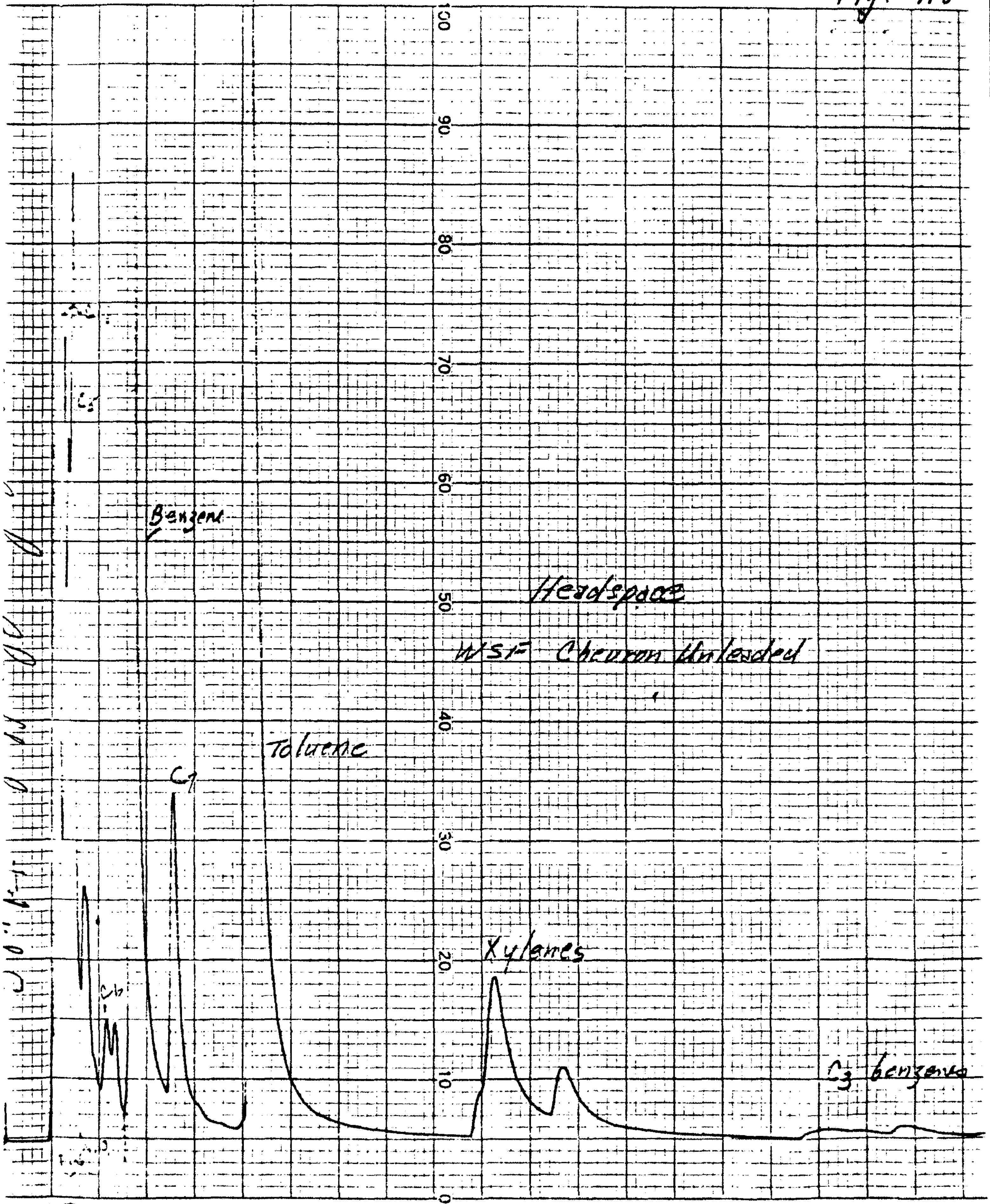


Fig. A 7



Head space
WSF Shell Super
benzene
Toluene
Xylenes
C_4
C_5
C_6
0
10
20
30
40
50
60
70
80
90

Fig. A8



LNR 0100-0025

Fig. A9

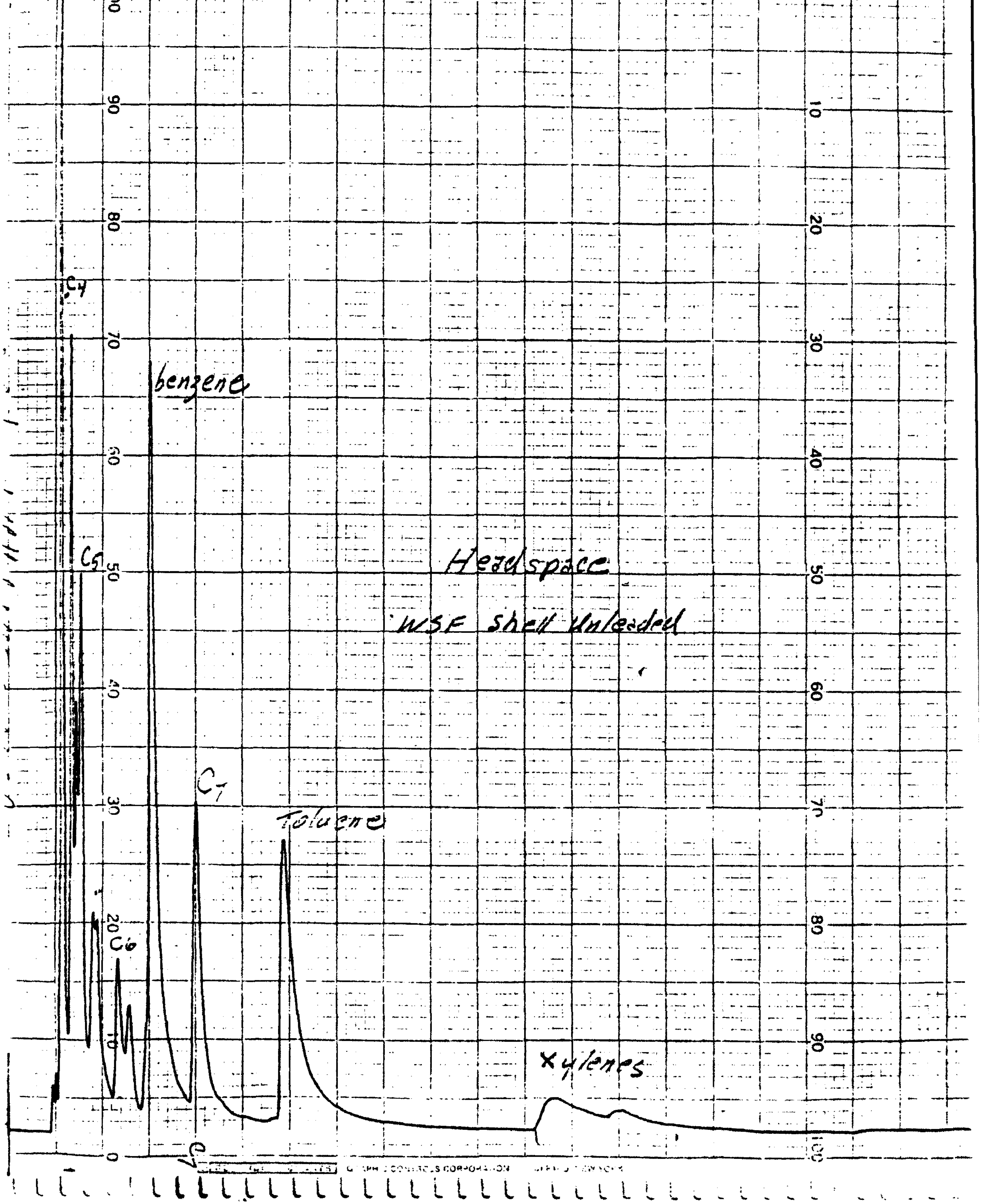

C4
C5
benzene
C6
C7
Toluene
Headspace
WSF Shell Unleaded
Xylenes

Fig. A10

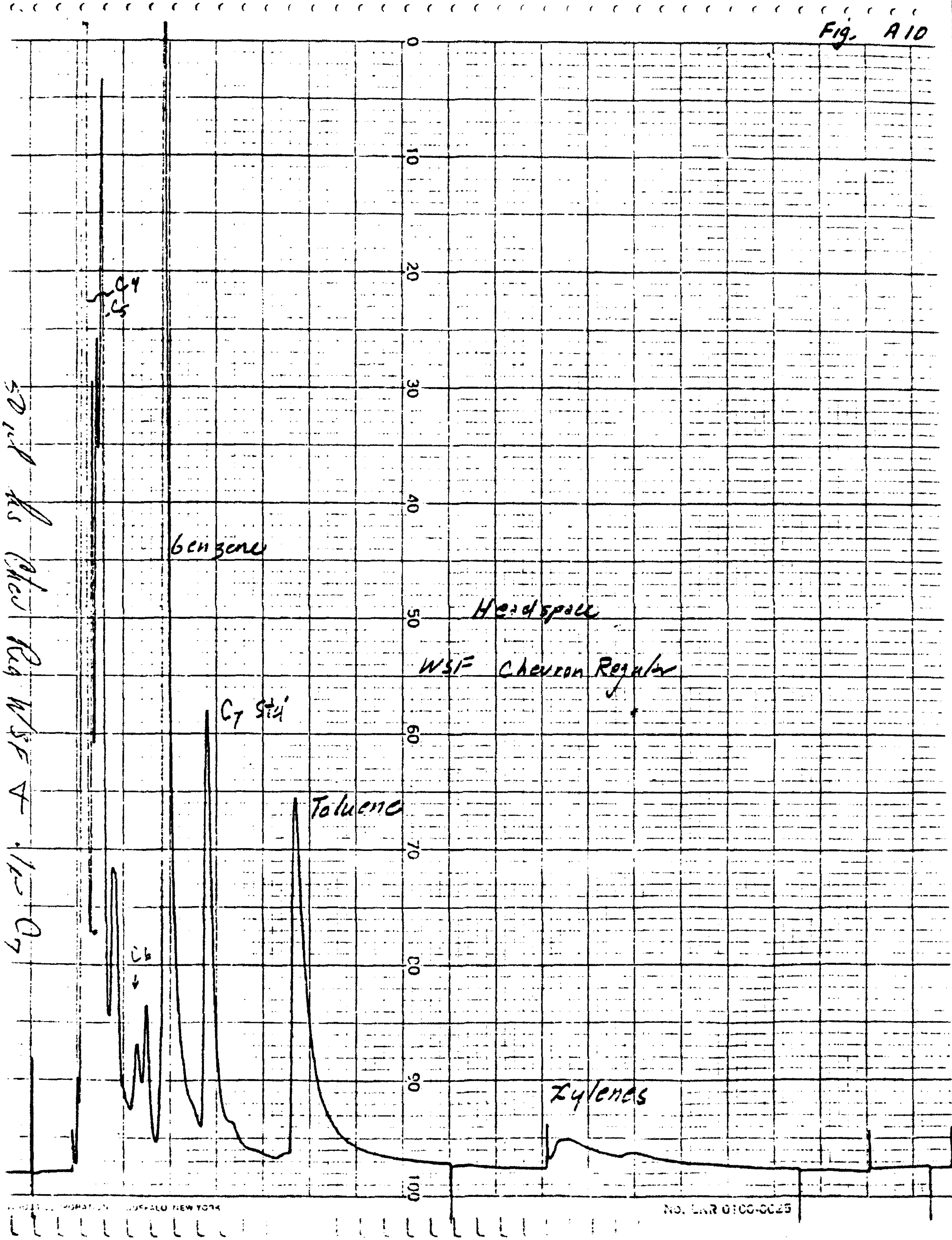
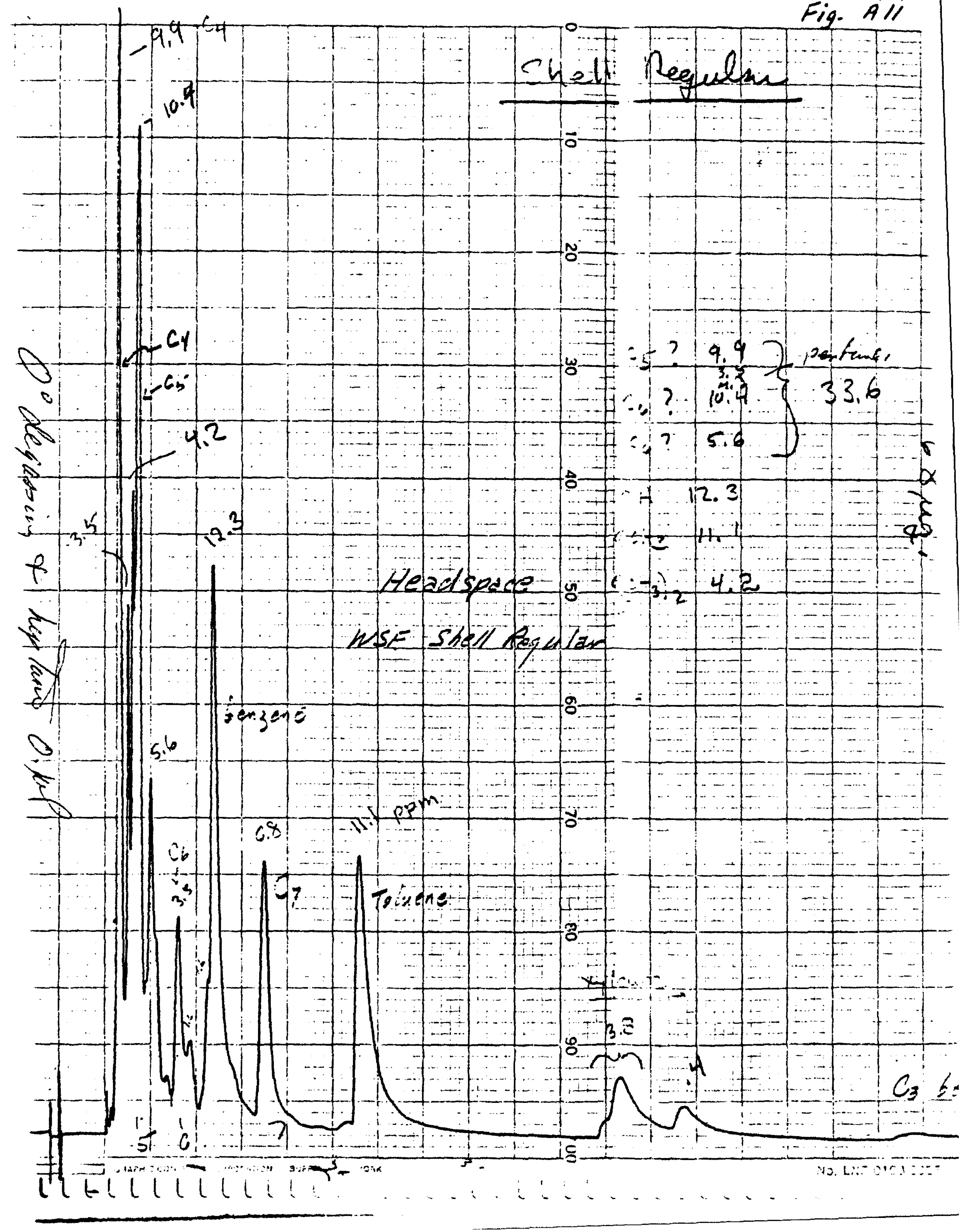
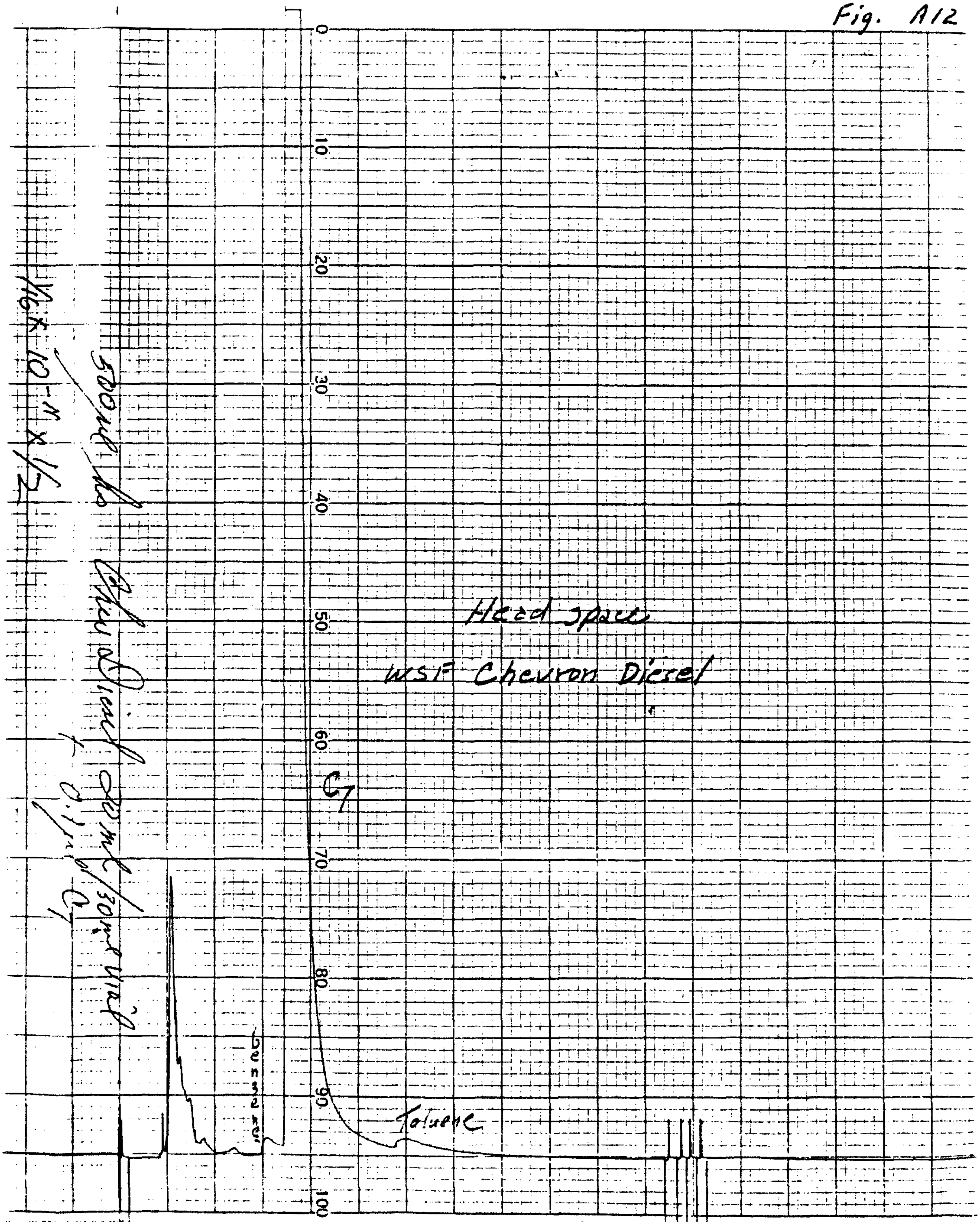

C4
C5
benzene
Headspace
WSF Chevron Regular
C7 Std
Toluene
C6
Xylenes
50 µl hs Chev Reg WSF + 1/µ C7
0
10
20
30
40
50
60
70
80
90
100
CORPORATION BUFFALO NEW YORK
NO. LAR 0100-0025

Fig. A11



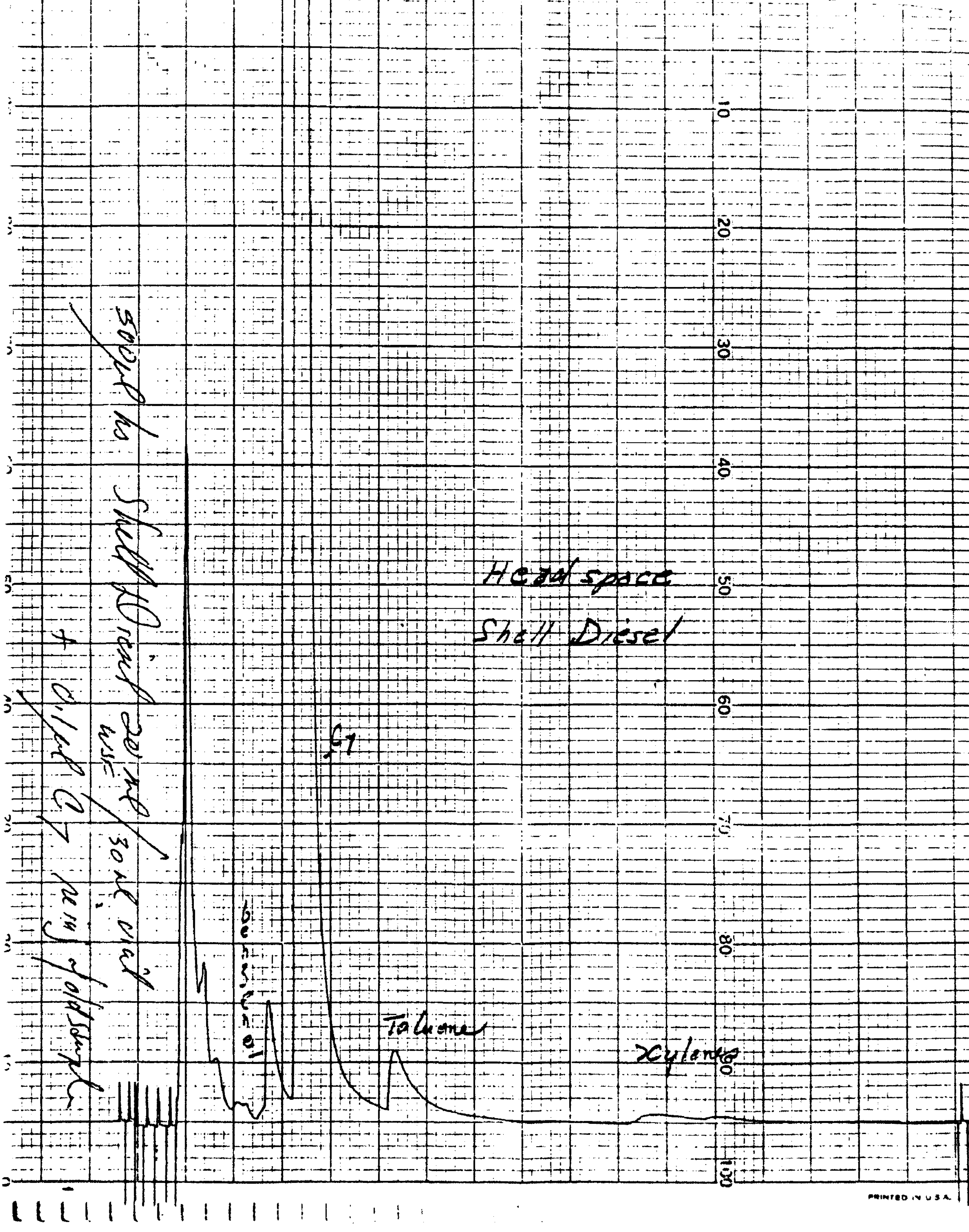
Shell Regular
9.9
C4
10.4
C4
C5
4.2
3.5
12.3
Benzene
5.6
C6
3.3
6.8
C7
11.1 ppm
Toluene
Headspace
WSF Shell Regular
0° degassing + heptane 0.1 ml
9.9
10.4
5.6
pentanes
33.6
12.3
11.1
4.2
3.8
.4
C3

Fig. A12



0
10
20
30
40
50
60
70
80
90
100
Head space
WSF Chevron Diesel
C7
Toluene
1/16 x 10^-11 x 1/2
BUFFALO NEW YORK
No. LNR 0100-0025

Fig. A 13



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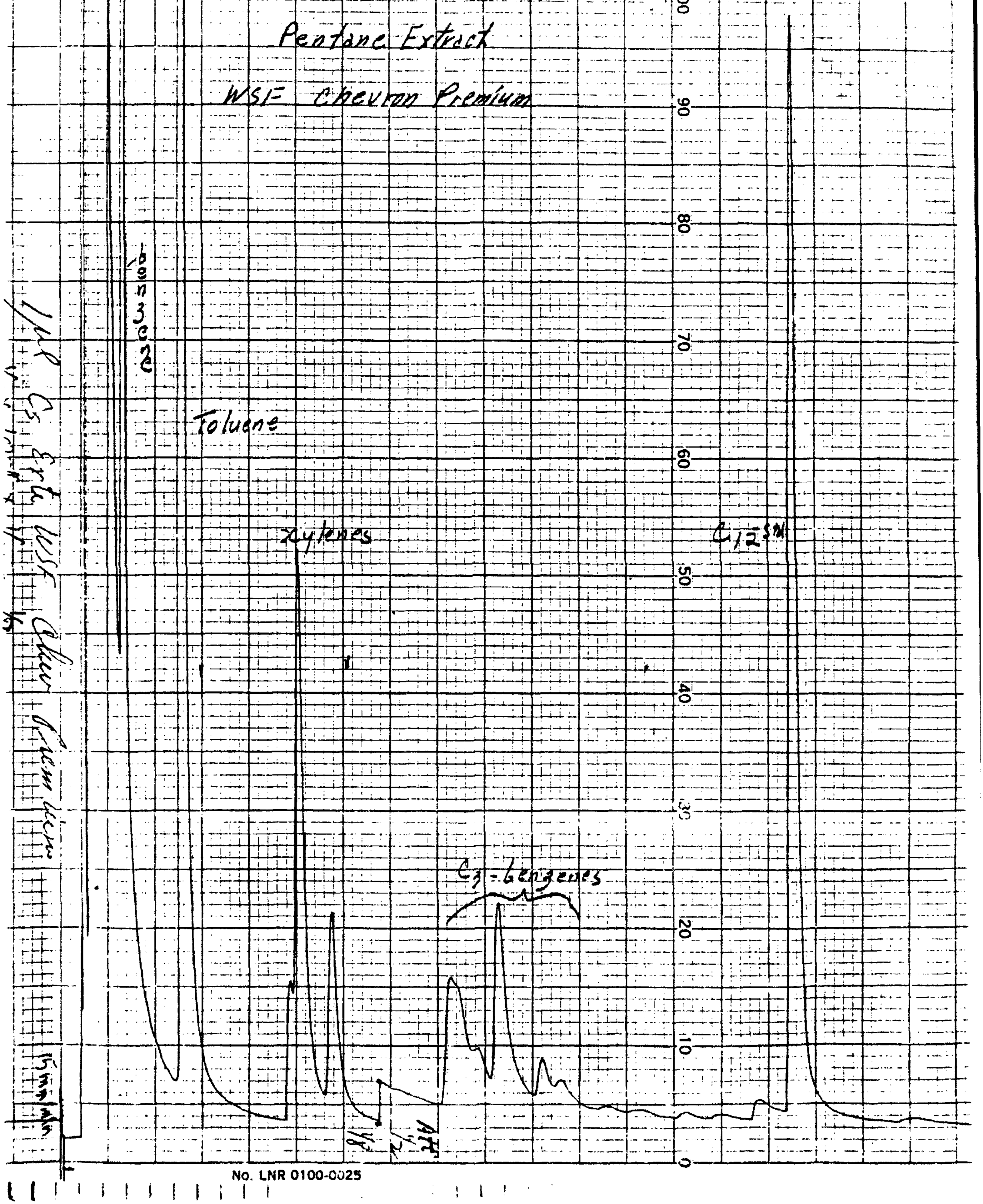

Pentane Extract
WSF Chevron Premium
Toluene
Xylenes
C_{12} std
C_3-benzenes
100
90
80
70
60
50
40
30
20
10
0
No. LNR 0100-0025

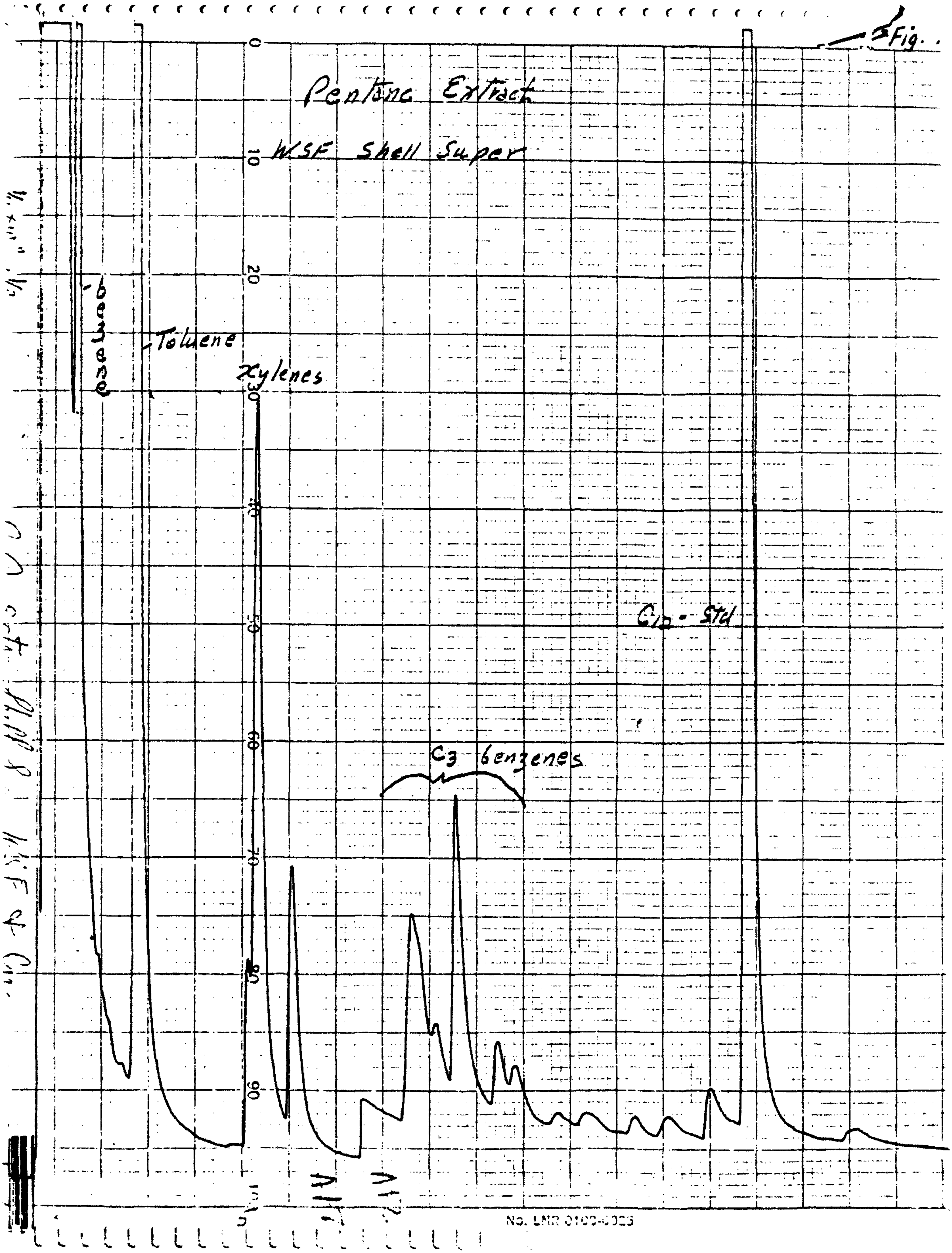
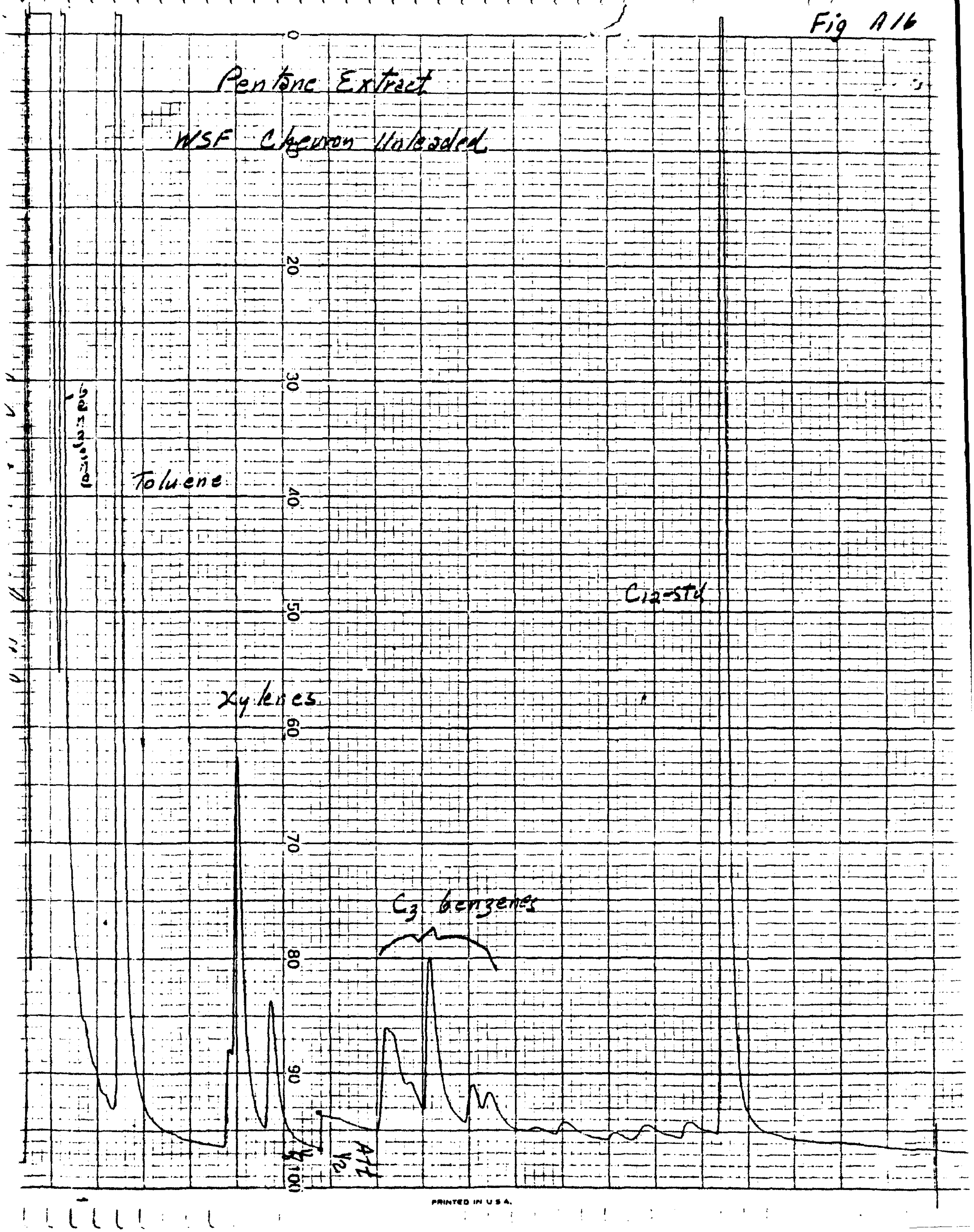
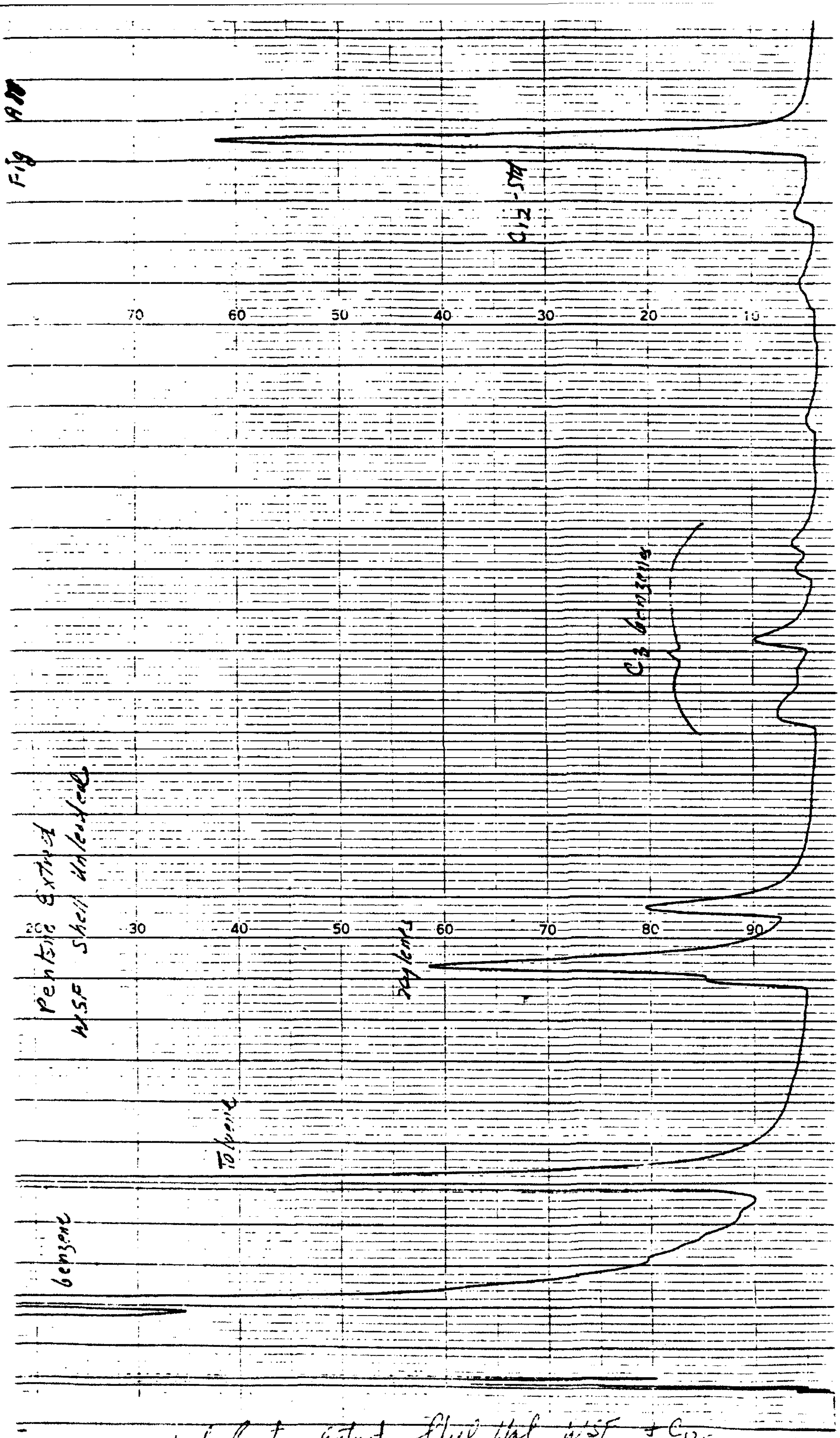


Fig.
Pentane Extract
WSF Shell Super
benzene
Toluene
Xylenes
C_3 benzenes
C_{12} - Std
0
10
20
30
60
70
90
NO. LNR 0100-0025

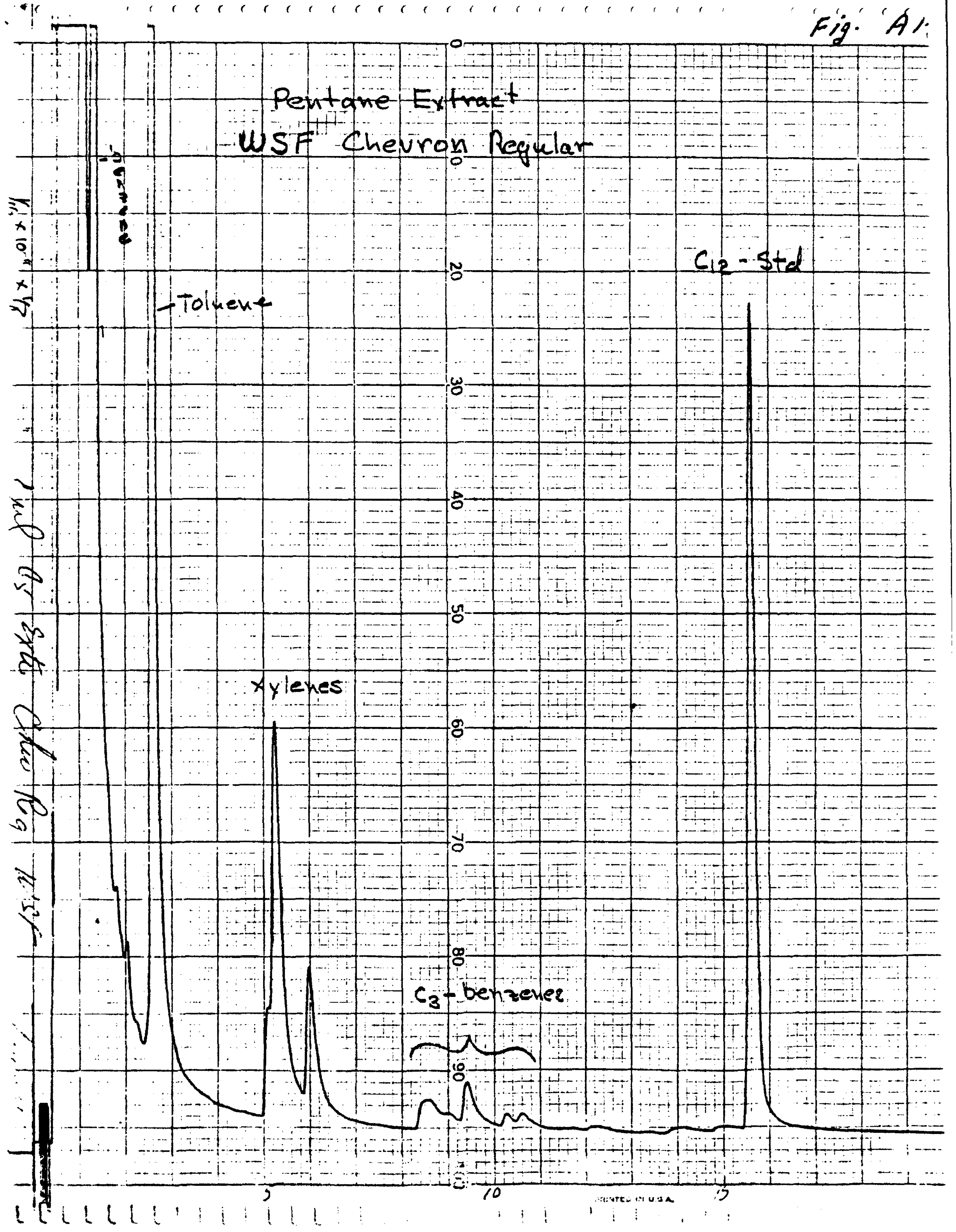
Fig A16


Pentane Extract
WSF Chevron Unleaded
Toluene
Xylenes
C3 benzenes
C12-std
ATT 1/2
0
20
30
40
50
60
70
80
90
100
PRINTED IN U.S.A.



1ml Pentane Extract Shell Unl WSF + C_{12}

Fig. A1.



Pentane Extract
WSF Chevron Regular
Toluene
Xylenes
C_{12} - Std
C_3 - benzenes

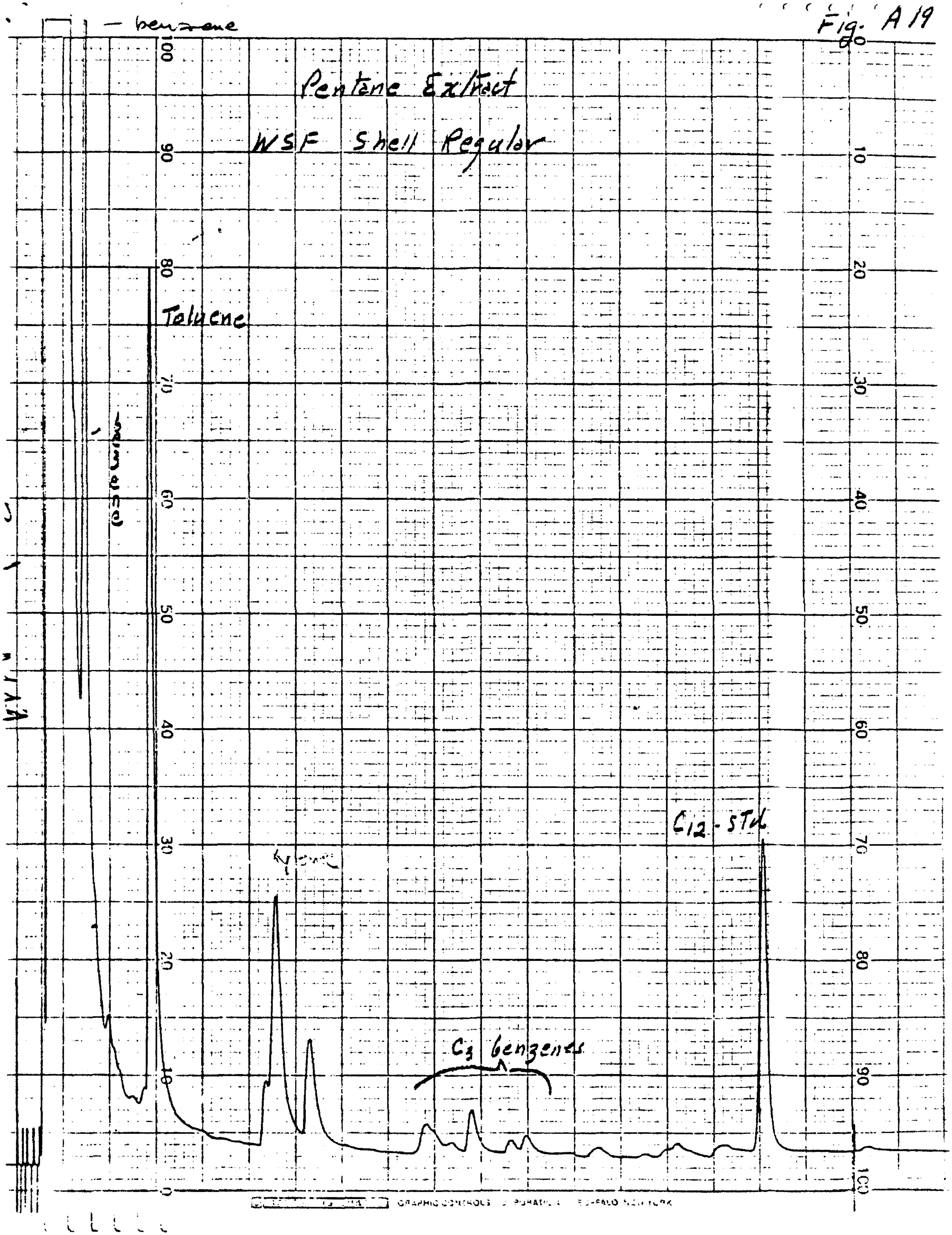

benzene
Pentene Extract
WSF Shell Regular
Toluene
C12 - STd
C3 benzenes
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
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Fig. A 19

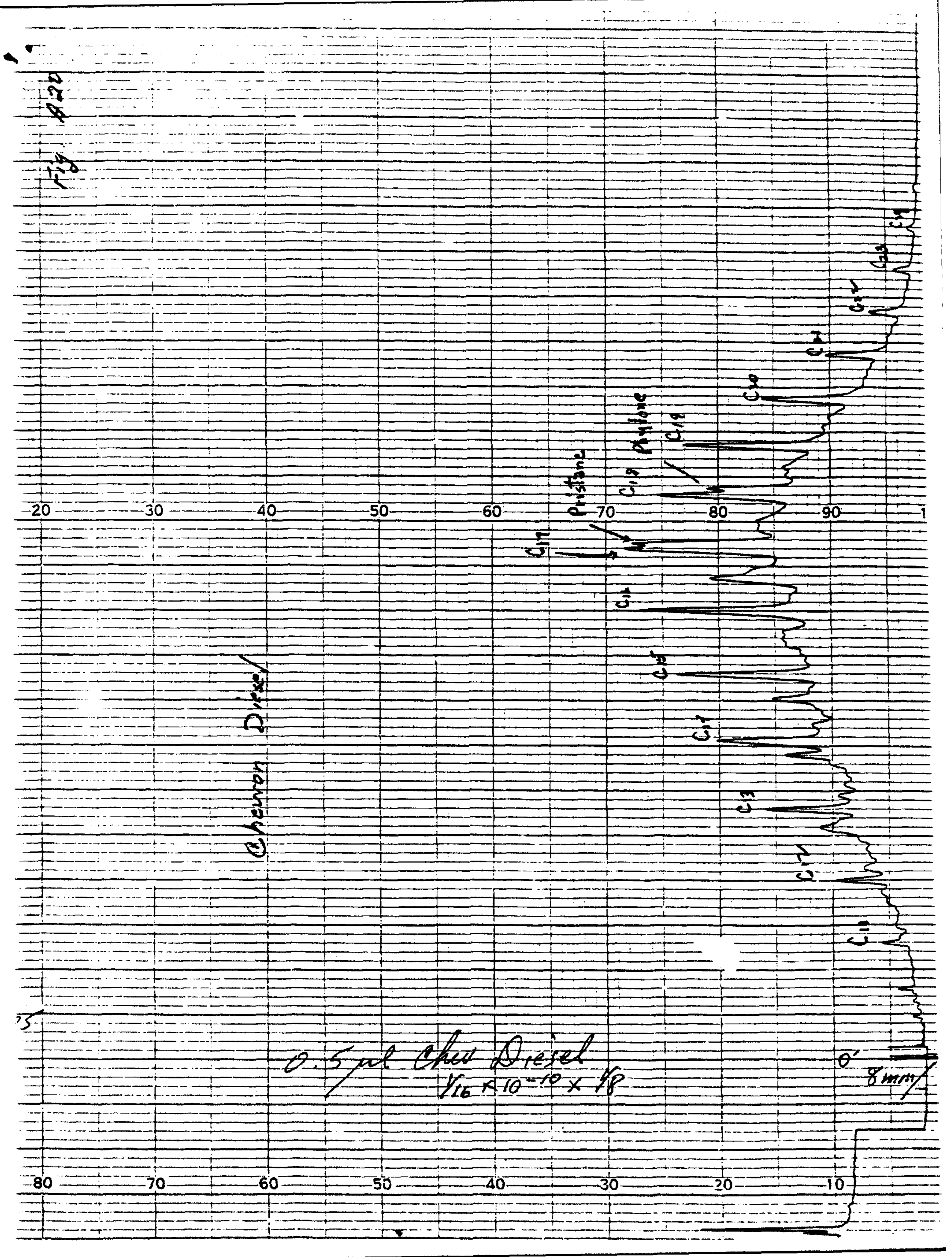
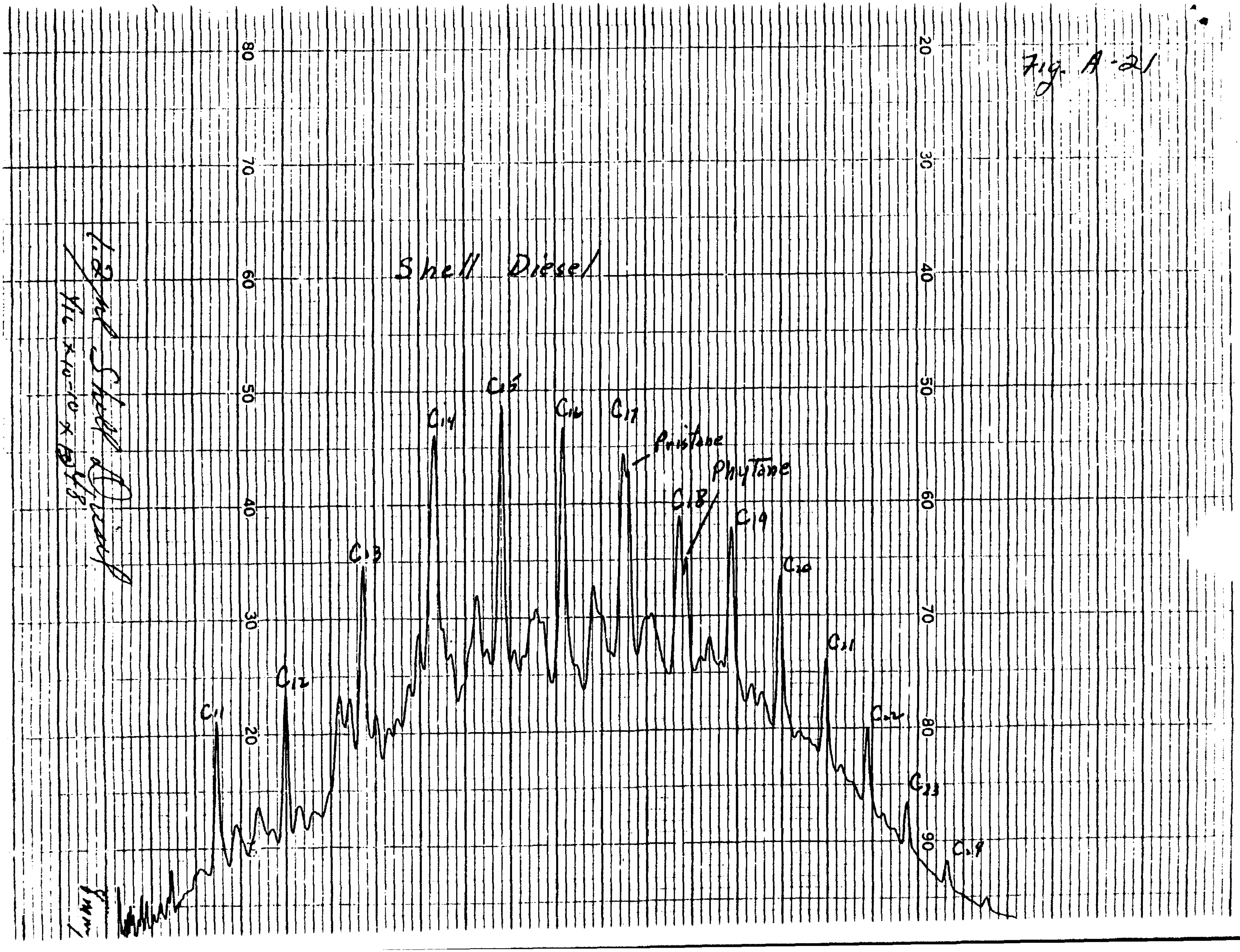


Fig A20
Chevron Diesel
Pristane
Phytane
0.5 µl Chev Diesel
1/16 × 10^-10 × 1/8
8 mm/
20
30
40
50
60
70
80
90
10

Fig. A-21


Shell Diesel
1.2 ml Shell Diesel
4/16 x10-10 x 48
8 mm/
C11
C12
C13
C14
C15
C16
C17
Pristane
C18
Phytane
C19
C20
C21
C22
C23
C24